













## EXPERIMENTAL STUDY OF GASES



# STUDY OF GASES

—AN—

ACCOUNT OF THE EXPERIMENTAL METHODS INVOLVED IN  
THE DETERMINATION OF THE PROPERTIES OF GASES,  
AND OF THE MORE IMPORTANT RESEARCHES  
CONNECTED WITH THE SUBJECT

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WITH AN INTRODUCTORY PREFACE

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## INTRODUCTORY PREFACE

THE manipulation of gases has been the object of attention at various epochs of chemical history. Scheele collected his gases in bladders; Priestley, unconsciously imitating Mayow, brought the pneumatic trough into use; and Bunsen devised processes still employed in analysis of gases. The device of Sprengel's pump, and later that of Töpler, has placed a new instrument at the disposal of chemists; and the ingenious methods of Hampson and Linde of producing liquid air in quantity has made it possible to deal with gases as easily, if not more so, as with liquids. In the research on the gases of the helium series a number of workers, including Lord Rayleigh, and Drs. Collie and Travers, have made use of apparatus, a description of which does not always appear in the original papers on the subject, but which will be found treated of in this volume. Dr. Travers has also taken the opportunity of tabulating the more important constants relating to gases; and what is perhaps of still greater moment, of directing the attention of chemists and physicists to lacunæ in knowledge, which suggest subject for research.

WILLIAM RAMSAY.



## PREFACE

IN the following pages I have attempted to give an account of the experimental methods which have been applied to the study of gases, and to describe the more important researches which have been carried out with a view to determining their properties.

It is probable that in no other section of chemistry or physics do such discrepancies occur as exist among the experimental values assigned by different investigators to the physical constants relating to gases. The existence of such irregularities renders the treatment of the subject rather difficult; and as in many cases the methods of manipulation, and the manner in which the gases experimented upon were prepared, are only briefly described in the original papers, it is often impossible to arrive at the probable sources of error. In stating results I have in many instances attempted to indicate to what extent they may be relied upon.

The breadth of the subject does not permit of its complete treatment within the limits of a single volume. I have therefore been obliged to restrict myself to a description of such methods as may find application in research, and of those investigations which either involve new principles, or which lead to results of importance. In the chapters which deal with the liquefied gases, of which our knowledge is daily increasing, statements are made which may shortly need revision. This is particularly the case with regard to experimental results which involve measurements of



temperature, for until we arrive at a more certain knowledge of the relationship between the practical thermometric and thermodynamic scales of temperature, the values of physical constants at low temperatures must retain a more or less empirical character.

A considerable portion of the book is devoted to the description of the methods which have been developed during the investigation of the gases of the helium group, and which are capable of application to the study of other problems. The opening up of this new field of research we owe to Professor William Ramsay, and I take this opportunity of thanking him for that training and experience in experimental science which I have gained while working with him at University College.

To Professor J. Norman Collie, to Mr. E. C. C. Baly, and to Dr. F. G. Donnan, I am much indebted for the advice and assistance they have rendered me. I also wish to express my most sincere thanks to Mr. George Senter, B.Sc., for revising the final proof-sheets of the book.

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## THE FUNDAMENTAL GAS LAWS

MATTER in the gaseous state is capable of completely filling all available space, and, except so far as gravity is concerned, of distributing itself equally through that space. It is, therefore, necessary to consider the conditions under which a gas is confined, in order to determine its quantity volumetrically.

The two fundamental laws which connect the volume of a gas with the temperature and pressure under which it is confined, are as follows:—

*The volume of a gas varies inversely as the pressure exerted upon it (Law of Boyle and Mariotte)—*

$$pv = p_0v_0$$

*The volume of a gas at constant pressure increases or decreases by  $2\frac{1}{3}$ , or 0·003665 of its volume at 0° C., for every degree Centigrade through which it is heated or cooled (Law of Gay-Lussac).* Thus, if we reckon temperature from  $-273^\circ$  C., the absolute zero, combining the two laws:—

$$\frac{pv}{T} = \frac{p_0v_0}{T_0}$$

In order to obtain comparative measurements it is necessary to reduce the observed volume of a gas to its volume under standard conditions. The standards which have been adopted for convenience are  $0^\circ$  C., the melting-point of pure ice, and the pressure equivalent to 760 millimetres of mercury at  $0^\circ$  C. in latitude  $45^\circ$ . This is equivalent to  $1\cdot0136 \times 10^6$  dynes per square centimetre, in absolute measure (see p. 117).<sup>1</sup>

<sup>1</sup> The ratio of the values of the gravity constant in the basement of University College, London, and at sea-level in latitude  $45^\circ$  is as 1 to 1·0066.



In dealing with mixtures of gases, each gas may be considered as exerting a pressure, dependent only on the quantity of it which is present in the mixture. The pressure exerted by a gaseous mixture is the sum of the partial pressure of the constituent gases—

$$P = p_1 + p_2 + \dots$$

It is also necessary to assume Avogadro's hypothesis, founded on Gay-Lussac's law of volumes, in order to connect the chemical and physical properties of gases. *Equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules.*

The general equation,

$$\frac{Pv}{T} = \frac{P_0 v_0}{T_0}$$

can be given a simpler form if we suppose the symbols on the right-hand side to represent the unit volume of gas under standard conditions of temperature and pressure, unit volume being taken to be 22.39 litres, the volume of one gram molecule of any gas

$$Pv = \frac{P_0 v_0}{273} T = RT,$$

$$\therefore 760 \times 22.39$$

If we express the pressure in atmospheres, the value of  $R$  in litre-atmospheres becomes

$$R = \frac{22.39}{273} = 0.0819,$$

$$\left| \quad PV = 0.0819 T. \right.$$

This equation finds wide application in the study of the properties of gases.

These laws hold true only within the limits of ordinary experimental research, and must not be taken to express the relationship between volume, temperature, and pressure over wide ranges. The deviations from the general laws will be considered later.

## • CHAPTER II

### MERCURY-PUMPS

Older form of pumps. Geissler's pump. Töpler's pump.—Accidents to pumps.  
Baly's pump. Shortened lift-pump. Automatic working of lift-pump.  
Sprengel's pump. Multiple-fall Sprengel's pump.—Production of high vacua.  
Surface condensation of gases. Methods of purifying mercury and of cleansing glass apparatus.

THE operations involved in the determination of the chemical and physical properties of gases consist for the most part in transferring quantities of gas from one piece of apparatus to another. If the gas under investigation can be obtained without difficulty and in large quantity, it is a matter of little importance whether any quantity of it be lost or contaminated. Recently, however, the investigation of the "rare gases," which can only be obtained in small quantity, has rendered it necessary to construct apparatus to enable the whole of the gas to be collected in a state of purity at the end of each experiment.

In recent years the introduction of improved forms of mercury-pumps has rendered work of this kind possible, and the removal of a quantity of gas from one piece of apparatus to another, without measurable loss or appreciable contamination, has become a simple matter.

Mercury-pumps may be considered as falling into two classes: lift-pumps, in which the gas in the pump-chamber is expelled by the upward motion of the mercury, and pumps of the Sprengel type, in which the mercury falling in drops down a capillary tube carries the gas with it, expelling it at the lower end.

The lift-pump finds its origin in the discovery of the principle of the barometer by Torricelli in 1643. In its earliest form a funnel, closed by a glass plate, was filled with mercury and

inverted so that the mercury ran into a basin, leaving the funnel vacuum. Later, a globe connected with a two-way steel stop-cock at the top, and below with a fall-tube bent on itself, and terminating in a funnel, was employed. The globe was filled with mercury through the funnel; the stopcock was turned so as to expel the air and then closed. The mercury was then allowed to run out at a tap at the bottom of the fall-tube, and so produce a vacuum in the globe; the two-way tap was then turned so as to place it in communication with the vessel to be exhausted. These operations were repeated till the limit of exhaustion was reached.

The first important improvement in the instrument consisted in replacing the U-tube, tap, and funnel by a flexible limb and reservoir, and finally, by a rubber tube and reservoir. Subsequently the steel two-way stopcock was replaced by one of glass, sealed directly to the pump-chamber (Fig. 1).

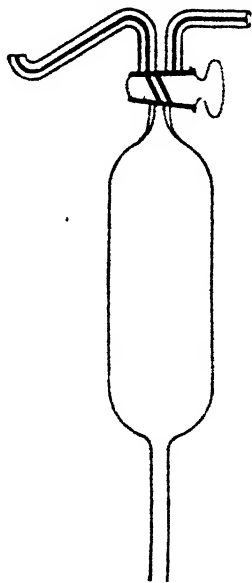


FIG. 1.

From the time of its introduction up to the middle of the present century, the mercury-pump held alternately with the mechanical air-pump, as the result of successive improvements in one or the other, the position of being the best means of producing a vacuum. The lift-pump, with the simple two-way stopcock, was incapable of becoming a very efficient machine on account of difficulties connected with the construction of the tap.

Since mercury does not wet glass, its capillary action is negative, and it is necessary to exert pressure in order to force it into small cavities. In consequence of this the mercury in its upward passage through the stopcock does not remove the air contained in the irregularities which must necessarily exist about and below the hole bored in the plug.

In the Geissler pump (Fig. 2) an attempt was made, and with some considerable success, to overcome this difficulty by means of an arrangement of three taps attached to the pump-head.

The plug of the tap  $t_1$  was pierced in the form of a flattened

cone, so that the pump could be placed in communication either with the side-tube connected with the vessel under exhaustion, or with the atmosphere.

During the early stages of exhaustion, the taps  $t_2$  and  $t_1$  remained permanently open. When no more air could be moved by simple exhaustion, owing to the irregularities which existed about the plug of the stopcock  $t_1$ , the taps  $t_2$  and  $t_1$  were brought into action. Mercury was first allowed to run through the whole system of taps; the upper one was then closed and the reservoir lowered till the mercury fell below the level of the lower stopcock. The air which had previously been retained about the two

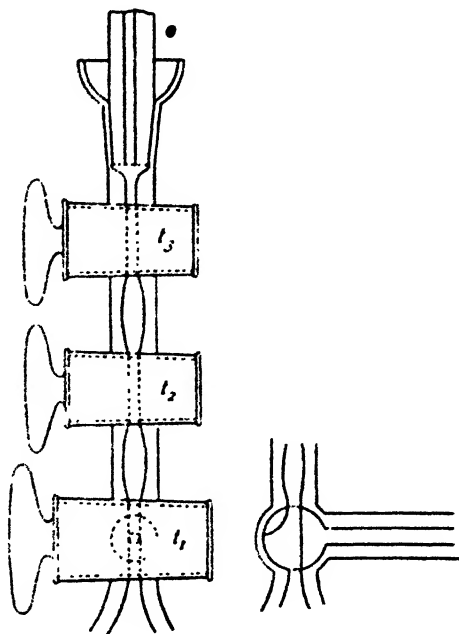


FIG. 2.

lower stopcocks, now filled the whole space above the mercury at much reduced pressure. The reservoir was then raised so as to drive this air into the space immediately below the upper stopcock. The middle stopcock was then closed, and the operation repeated. The whole of the pump-chamber was in this way so far freed from traces of air, as to render it possible to produce a much higher vacuum than could otherwise have been attained to.

This ingenious but clumsy apparatus has now given place to pumps of simpler construction, in which stopcocks, the cause of the whole difficulty, are entirely dispensed with.

In order to attain maximum efficiency the pump should be so constructed that the rising surface of the mercury comes in contact with a continuous surface of glass only. Taps, or ground-glass junctions, must be avoided, as they are certain to lead to the retention of small quantities of air, and so render the production of high vacua impossible.

*The Topley pump.*—In many of the operations which will be

described later it is necessary, not only to remove a quantity of gas completely from a vessel, but also to collect the gas without loss, and free from admixture with air. The Töpler pump (Figs. 3, 4) satisfies these conditions, and possesses the additional advantage of being simple in construction and easily repaired when broken. For laboratory use the following measurements

have been found convenient, but the general dimensions may, of course, be varied with regard to the work in view; the efficiency of the instrument will, however, depend upon the attention which is paid to certain *details* in its construction.

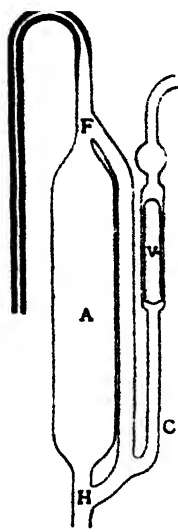


FIG. 3.

The pump-chamber A (Fig. 3) is made of stout glass, and should be about 200 mm. long and 50 mm. in diameter; the ends, and particularly the upper end, should be tapered considerably to meet tubes of about 13 mm. in diameter. If the upper end of the pump-chamber presents a surface approaching to the horizontal to the mercury as it rises to the pump-head, films or even bubbles of air may be entrapped between the mercury and the glass, and exhaustion will be slow. The side-tube, which joins the vertical tubes at F and H, should also be of about 13 mm. diameter; the internal angle between the two tubes at the upper junction should, for the reasons given above, be very acute. The tube C, through which the gas enters the pump, should be much narrower than the side-tube, 4 mm. is a convenient diameter; if it is not made so the gas which enters the pump while the mercury is still falling, may carry the whole of the mercury in the side-tube into the upper part of the pump, and cause a serious fracture. If the pump is properly constructed, the gas will rise in bubbles between the mercury and the glass.

The vertical tube F at the top of the pump-chamber, should be tapered to meet the capillary tube G, which should be bent on itself in a continuous curve of about 3 cm. in diameter immediately above this point. The length of the capillary tube should be about 800 mm., and its internal diameter should not much exceed 1 mm.; it should be turned up at its lower end so as to admit of collecting gases through the pump. The capillary tube may

easily be replaced when broken if a sufficient length of tube is left above the junction at F. A piece of tube, of the same diameter as the vertical tube of the pump, is first sealed to a straight piece of capillary tube of sufficient length. The tube is worked in the blowpipe flame till a perfectly even tapered junction is obtained: it is then bent, cut to the right length, and sealed to the pump-head with the aid of a small blow-pipe. The efficiency of the pump will depend to a great extent on the care which is expended on this part of it.

The lower vertical tube should be so long, about 800 mm., that when there is a vacuum in the pump and the mercury stands below the level of the joint H, the lower end of it lies below the level of the mercury in the reservoir, or air may slowly leak into the pump through the junction with the rubber tube. The rubber tube should not be longer than is necessary to allow of the reservoir being raised to the level of the pump-head, and its internal diameter should be nearly as large as that of the glass tube to which it is attached, so as to allow of the free flow of the mercury. In order to obviate any chance of the rubber tube bursting, it should be sewn into a strip of leather or enclosed in a piece of hollow cotton lamp-wick.

In order to prevent the mercury from passing into the tube D, containing pentoxide of phosphorus, when the reservoir is raised, the tube C may be carried vertically upwards to a height of about 900 mm. and then bent on itself. It is more convenient, however, to employ a glass valve V as in the figure, and it is probable that the rate of exhaustion of a piece of apparatus attached to the pump would be considerably decreased by the interposition of the long glass tube. The valve should be ground so that its upper surface fits sufficiently accurately into the inner surface of the tube containing it to hinder the passage of the mercury: the angle between the two surfaces should be very obtuse, or the valve may tend to remain closed after the mercury has fallen. The top of the valve

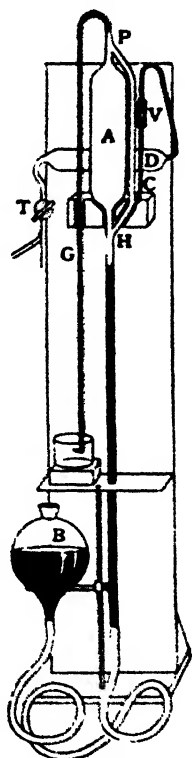


FIG. 4.

should be on a level with the junction P (Fig. 4), so that the mercury closes it before it reaches the capillary tube.

The tube D containing the pentoxide of phosphorus (see p. 41) is usually connected with a large two-way stopcock T, so that the pump may be used in connection with more than one piece of apparatus.

The pump may be fixed to a stout board as in the figure. The block H is cut so that the bottom of the pump-chamber rests on it, and is kept in place by means of a strip of brass and a couple of screws. The fall-tube passes through a hole in the bottom of the tray; a cork fitting closely to the fall-tube serves to keep it firmly in place, and to prevent the escape of mercury through the hole. The tray supports the basin into which the end of the capillary tube dips. The board to which the pump is attached may be screwed to the wall at a convenient height, or fixed to a stand.

The reservoir may be placed in a bracket, or supported in a retort ring with a piece cut out of it to allow of the passage of the rubber tube. The retort ring may be fixed to an iron rod passing through holes in the tray and stand. A pulley and cord may be found convenient in working large pumps.

*Method of working the Töpler pump.*—The pump is first carefully cleaned with chromic and sulphuric acids, washed with distilled water and alcohol, and dried. It is then set up on the stand, the tube C is sealed to the tube D, containing pentoxide of phosphorus, and the rubber tube and reservoir are attached. When sufficient mercury has been poured into the reservoir and trough the pump is ready for use.

The reservoir is raised so as to expel about two-thirds of the air in the pump-chamber through the capillary tube, and is then lowered. As the mercury falls the air in the tube containing the pentoxide forces its way through the mercury in the side-tube, and enters the pump. The operation is then repeated, but during the first few strokes the air should not be completely expelled from the pump-chamber. If this precaution is not taken the air will begin to enter the side-tube, while it still contains a long column of mercury; it will not then break up into bubbles, but will probably carry the whole of the mercury upwards against the junction F, causing a serious fracture. On no account should the tap T be opened while the mercury is falling in the pump-

chamber, or a similar accident may result. In any case the gas should only be allowed to enter the pump slowly. A rapid current of gas may impact the pentoxide of phosphorus into the end of the tube containing it, and render subsequent exhaustion very slow.

During the last stages of the process of exhaustion care must be taken that the mercury does not come into violent contact with the top of the pump, or a fracture may result. The mercury may be allowed to rise rapidly to the junction F; it may then be checked either by pinching the rubber tube or by lowering the reservoir. With practice the action becomes automatic.

When a pump is first set up it should be allowed to remain exhausted for a sufficient time for the complete absorption of water in the apparatus by the pentoxide of phosphorus. Further, since gases like carbon dioxide condense in considerable quantity on glass surfaces, the maximum efficiency will not be reached till the pump has been filled with air, and exhausted two or three times.

*Collecting the gas delivered from the pump.*—Gases removed from any vessel by means of the pump may easily be collected in a state of absolute purity. A tube filled with mercury (p. 26) is brought over the upturned end of the capillary tube, and the gas is delivered directly into it.

*Accidents.*—With ordinary care, a Töpler pump may be used for years without a serious accident. The capillary tube may be frequently replaced (p. 18), and so long as the crack does not extend into the T-joint any fracture about the upper part of the pump may be made good with the aid of a small blowpipe. Sometimes a crack appears in the capillary tube, and extends slowly along its entire length. The crack may commence either at the top or at the bottom of the tube; but as the crack does not appear to cause a leak, the pump may often be used for weeks in this condition. The cause lies, in all probability, in the vibration set up in working the pump; in some pumps capillary tubes may crack one after the other, in others no crack ever appears.

The tube containing pentoxide of phosphorus must be replaced as soon as the reagent becomes exhausted. It is essential to the efficient working of the pump that all moisture shall be completely absorbed.

In larger pumps the chamber is often made pear-shaped for



convenience. This form of pump (Fig. 5) has not, however, any particular advantage over the cylindrical form.

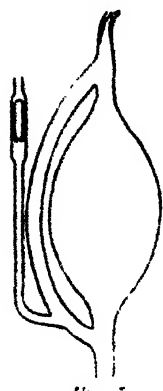


FIG. 5.

For the rapid production of high vacua in large vessels, when it is unnecessary to collect the gases, a pump invented by Mr. E. C. C. Baly has been found to give very good results (*Phil. Mag.* September 1894). The pump consists of three chambers connected by means of syphons, which have a small internal diameter. The tube *a* is connected with a reservoir, and the tube *b* through a long vertical glass tube or a valve to the apparatus under exhaustion. The tap *c* is connected with a water-pump which is kept running during

the whole exhaustion.



FIG. 6.

After preliminary exhaustion by means of the water-pump, the mercury is caused to rise in the pump till it flows into C: the mercury is then allowed to fall. The vessel C now contains air at the pressure of water vapour at the temperature of the water in the pump. B contains a Torricellian vacuum. A contains gas at low pressure. When the mercury again rises it drives the gas from the pump-chamber into the chamber B, and in order to prevent any quantity of gas from accumulating in B, the mercury is now and then allowed to rise so far as to fill the chamber. This, however, is only necessary during the early stages of the exhaustion. The upper chamber of the pump may be constructed like a Topley pump in order to collect the gas delivered through it.

*Shortened form of lift-pump.*—If the pump-chamber is large the work of lifting the reservoir will be considerable, even if the apparatus is fitted with a winch and cord. The following method has been worked with success, and obviates all labour in using the pump.

The pump and reservoir are fixed permanently in position, so that when the pressure is the same in each the mercury in the pump stands at about 10 cm. below the point of entry of the side tube. The connection between the two may be of glass.

The opening in the top of the reservoir is closed by a rubber stopper through which passes one limb of a two-way stopcock.

By means of the stopcock the interior of the chamber may be placed in communication with a water-pump or with the atmosphere; by turning the stopcock alternately one way and the other the mercury is caused to rise and fall in the pump-chamber. The apparatus must, of course, be partially exhausted by means of a Fleuss or water-pump before the automatic arrangement can be started.

This apparatus can be made to work absolutely automatically by means of a device designed by Mr. E. C. C. Baly. The tap *a* which is in communication with the mercury reservoir *b*, with a water-pump, and with the atmosphere, can be turned through an angle of



FIG. 8.

90° by means of the mechanical arrangement shown in the figure. The beam *cd* rotates about the point *c*, and carries at the end *c* a weight, and at *d* a cup which can be filled with water by means of a flexible tube attached to it, or emptied by means of the syphon *f*. The rate at which the reservoir fills is regulated by the time required for the mercury to rise and fall in the pump. When the cup is empty the end *d* of the beam rises and places the mercury reservoir *b* in connection with the water-pump; the mercury then falls in the mercury-pump. In the meanwhile the cup is filling with water, and when its weight becomes greater than that of the counterpoise at *c*, it falls, turning the tap *a*, so as to admit air into the mercury reservoir *b*. The syphon *f* is so regulated that at the moment that the mercury has completely expelled the air from the pump-chamber it empties the cup. The tap *a* is then again automatically turned, and the process repeats itself.

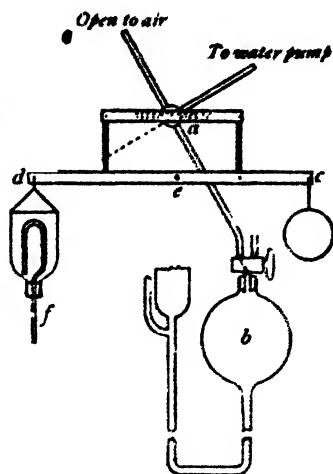


FIG. 7.

*The Sprengel pump.*—Mercury-pumps of the type introduced by Hermann Sprengel in 1865 are still extensively employed by manufacturers of glow-lamps and for

other purposes. In its simplest form the mercury falls in drops down a capillary tube, carrying with it air from a side-tube which is sealed to the vessel under exhaustion (Fig. 8). This pump was employed by Graham in his researches on the diffusion of gases.

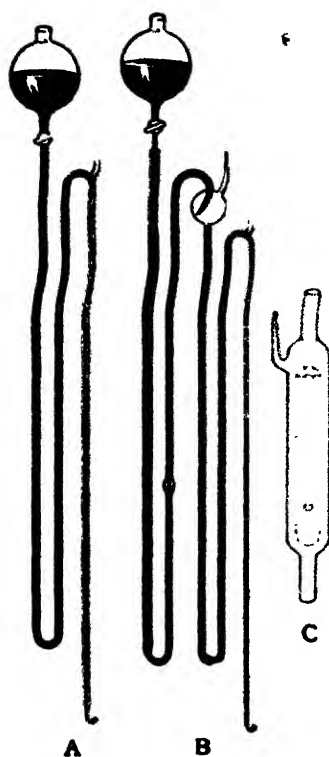


FIG. 9.

and pump-head (Fig. 9, B). The mercury passes from the reservoir to the top of the exhausted globe through an inverted syphon, and enters the globe through a jet, which is slightly bent to one side. The stream of mercury impinges against the side of the globe, and falls in small drops into the first limb of the second inverted syphon, which carries it to the pump-head. The globe may be exhausted by means of a second pump, and permanently sealed, and after working for months only a minute quantity of air will have accumulated in it. This addition renders it possible to attain a higher degree of exhaustion than by any other means.

*The pump-head.*—In the earlier forms of Sprengel pump the

The main difficulty to be contended with in working the pump was due to the bubbles of air carried down by the mercury from the funnel. This was only partially overcome by the introduction of an inverted syphon between the funnel and pump-head only. An arrangement introduced by Osmund in 1874 in which the mercury entered the first limb of the syphon through a long narrow tube leading nearly to the bottom of it is a distinct improvement, and air traps (Fig. 9, B, C) placed in the ascending limb of the syphon are very effective, but none of these methods are quite satisfactory.

The solution of the difficulty has been found in the introduction of an exhausted globe between the reservoir

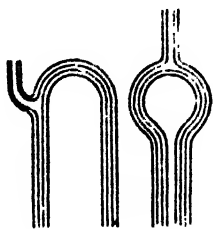


FIG. 10.

side-tube was set into the vertical fall-tube at an angle slightly inclined upwards. Later the introduction of the syphon led to placing the tube near the top of the fall-tube. Either of the forms shown in Figure 10 answer satisfactorily.

A mercury injector has been used in connection with single-fall Sprengel pumps, but the results are not better than those obtained by means of the simpler form.

To prevent the return of the gas which is carried by the mercury down the fall-tube, and which during the last stages of the exhaustion is too minute in quantity to form bubbles, Mees (1875) introduced a bend in the fall-tube (Fig. 11) just below the point at which the column of mercury becomes continuous. The gain is not, however, as great as might be expected, and the liability to breakage is many times increased.

The length of the fall-tube should be about 900 mm., and it should have an internal diameter of about 1.5 mm.; the lower end may be bent upward in order to allow of gases being collected.

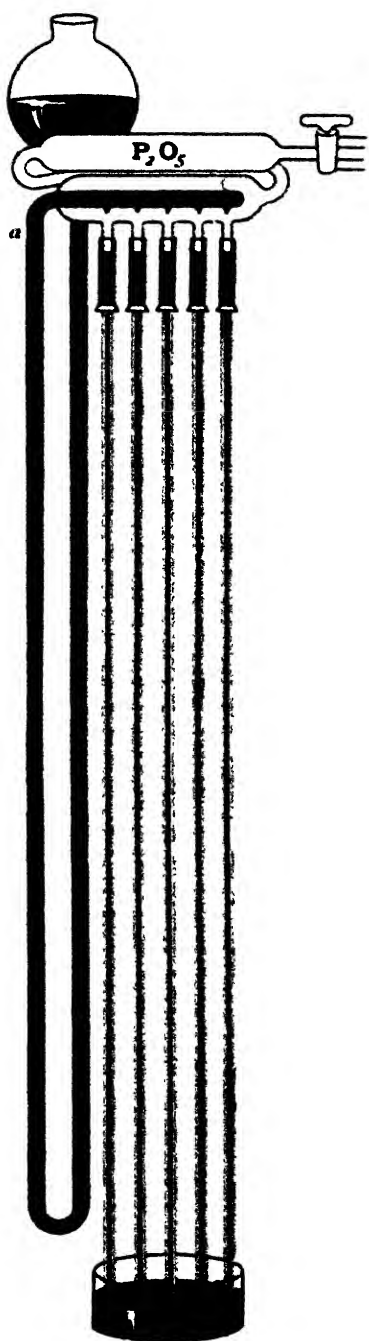


FIG. 11.

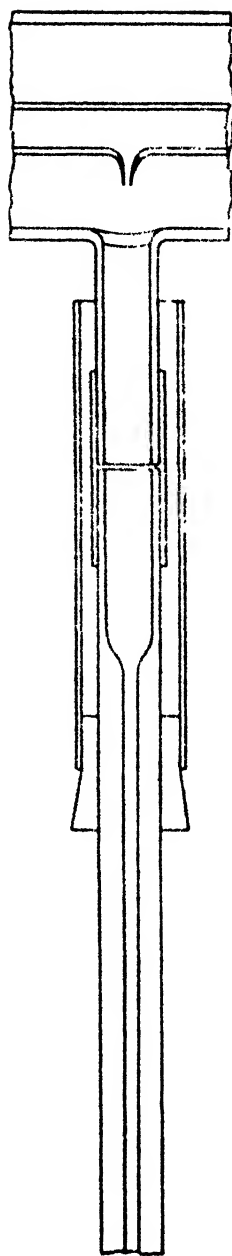
*The multiple-fall Sprengel pump.*—Sprengel pumps with more than one fall-tube have been, and still are, largely used. A simple form with five fall-tubes is shown in Fig. 12 A. The mercury from the reservoir is brought to the pump-head by an arrangement of tubes similar to that already described, and falls into the capillary tube from jets in the tube *a*. The capillary tubes need not be sealed to the pump-head, but may be joined to it, as in Fig. 12 B, by rubber tubes protected by mercury cups. It is important that the jet should lie directly over the top of the capillary.

Gimingham's pump has seven fall-tubes which are sealed directly to the pump-head (*Proc. Roy. Soc.* 1876; *J. Chem. Indust.* 1884).

A shortened form of Sprengel pump (Fig. 13) was first introduced by Nicol. The mercury falls from jets in the tube *a*, as in Fig. 12, into the capillary tubes, which are short and pass into a vessel *b* connected with a water-pump and with a wide fall-tube of such a length that the mercury rises to a sufficient height in the vessel *b* to cover the lower ends of the capillary tubes. The gas removed by the Sprengel pump is delivered into the water-pump vacuum in *b*.



**A**



**B**

**FIG. 12.**

One of the chief difficulties in the practical working of the Sprengel pump lies in the formation of mercurous oxide in the fall-tube at the point where the falling drops of mercury strike the top of the permanent column. This is only found to happen when the gas in the pump is air or oxygen, and is due to the formation of ozone and nitrogen oxides by the electrified mercury. Where only

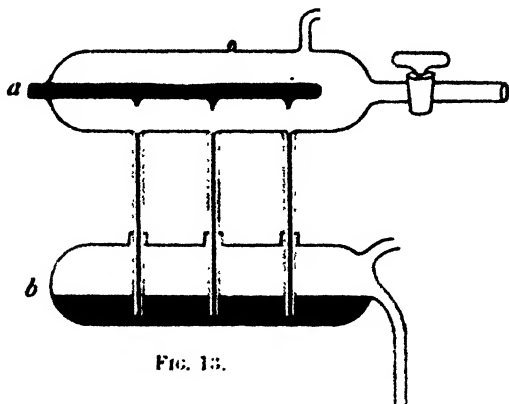


FIG. 13.

a moderate vacuum is required it will be found that the introduction of a few drops of sulphuric acid into the pump facilitates its action; in this case, however, the diameter of the fall-tube should be somewhat larger.

*Preliminary exhaustion of apparatus.*— Much time and labour may be saved by employing a Fleuss oil-pump or a water-pump for the preliminary exhaustion of pieces of apparatus. The double-cylinder Fleuss pump, when in good working order, will give a vacuum such as is required for the production of the X rays. A water-pump working with a head of water of thirty-five feet will reduce the pressure to the vapour pressure of the water passing through it. A good water-pump can only be obtained by testing a number of them against a mercury gauge and selecting the best.

*Methods of purifying mercury.*—After being in use for a long time mercury is sure to become contaminated with small quantities of lead, copper, zinc, or other metals with which it may come in contact. Copper is usually introduced when copper wire is used in securing rubber connections, small clippings of copper dropped accidentally on the table coming in contact with mercury; zinc and lead are usually present in commercial mercury. Several methods for the distillation of mercury have been described, but the process itself is inefficient in separating the volatile zinc.

Mercury which is not very impure may be easily purified by the following method. The dry mercury is poured into a tube as in Fig. 14, which should be about 5 cm. in diameter, about 80 cm. long, and which is inclined at a slight angle by means of blocks.

A gentle current of air is made to flow, by means of a water pump, over the surface of the mercury for about twenty-four hours. The impurities are quickly oxidised, and the pure mercury may be filtered off.



FIG. 14.

By allowing mercury to fall in a fine stream through a 5 per cent solution of nitric acid in a vertical tube, as in Fig. 15, it may be quickly freed from impurities. The pure mercury flows out through the capillary tube at the lower end, quite dry and practically pure. The acid should not be allowed to stand in the tube when not in use, as it will form a crust of the nitrate in contact with the residual mercury. The impure mercury can be fed in at the top through a funnel drawn out to a fine point.



FIG. 15.

When mercury is very impure it may be easily purified in the following manner. The mercury is placed in a stout filtering flask (Fig. 16) beneath a 5 per cent solution of nitric acid. A glass tube passes through the cork nearly to the bottom of the flask, and a current of air is caused to pass through the liquid by connecting the side-tube of the flask with a water-pump. The liquids are subsequently separated by a tap funnel, the solution of mercurous nitrate being returned to the flask for further use.

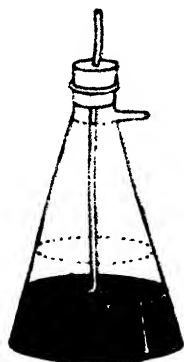


FIG. 16.

*Cleaning apparatus which has contained mercury*—When glass apparatus which has contained mercury has been in use for some time it is liable to become coated on the inside with compounds of mercury. If the gas which has been allowed to enter the apparatus has at any time contained sulphur compounds or traces of the halogens, the coating is sure to consist partly of sulphide or halides of mercury, which are almost impossible to remove by means of ordinary reagents. The following method has been found very efficient

in cleaning apparatus which has become very dirty through long use. Zinc dust is made into a thin paste with water, and

the liquid is poured into the apparatus, which is shaken so that the sides become well covered with the zinc. Dilute hydrochloric acid is then added, and the apparatus is again well shaken and finally washed out with water. The insoluble mercurous compounds are now reduced to metallic mercury which can be removed with a little strong nitric acid.



## CHAPTER III

### GAS-MANIPULATION; STOPCOCKS, ETC.

**Sealed-glass junctions—India-rubber connections—Ground-glass junctions—Method of connecting metal and glass tubes—Stopcocks—Three-way stopcocks.**

**SEALED-GLASS JUNCTIONS.**—It is often convenient, and sometimes absolutely necessary, to connect pieces of glass apparatus by sealing the leading tubes *in situ* in the blowpipe flame. If the tubes are of not more than one centimetre in diameter, the operation is an easy one, and may be carried out in the following manner.

The tubes are brought together so that the edges exactly coincide, and a piece of rubber tube is connected with a side-tube or stopcock leading to the interior of the apparatus, all the other openings are closed. The edges of the tube are first carefully heated in the luminous flame, and when thoroughly annealed the gas is turned down so that when the blast is turned on only a short section of the tube is heated. The junction must now be rapidly heated on all sides and the edges pressed together so as to leave no gap: if this is impossible, or if the glass shrinks back so far as to leave a gap, the junction may be completed by means of a thin rod of the same kind of glass and a very fine blowpipe flame. The junction should next be strongly heated so that the glass melts, the tube shrinks to about one-half of its original diameter, and is then blown out again by means of the rubber tube attached to the apparatus. This operation is repeated till all trace of a line of union disappears. The junction is then again carefully annealed in the blowpipe flame.

It is essential that the two glass tubes should be of the same kind of glass or, though it may be possible to seal them together, they will afterwards come apart. Further, it is sometimes impossible to manipulate old glass in the blowpipe flame, as it

devitrifies, becomes crystalline, and does not melt. Traces of dirt, and particularly of pentoxide of phosphorus, render it impossible to make a good joint, so that the tubes should always be washed out and dried before an attempt is made to seal them together. Tubes which have contained mercury appear to be somewhat difficult to manipulate, though the cause is not apparent.

In sealing capillary tubes together the ends should be blown into bulbs, and a very small flame should be used.

If the total capacity<sup>a</sup> of the apparatus is large, great care must be taken in blowing out the junction, and a wide rubber tube should be used. Since the pressure required to expand a bubble varies inversely as its diameter, the pressure required to expand the melted tube decreases as its diameter gets greater. Consequently, though it may be at first difficult to blow out the tube which has been melted down in the blowpipe flame, when once started, the pressure in the apparatus may be sufficient to expand it into a bulb, unless the side-tube is of sufficient cross-section to allow of its being quickly released. On the other hand, in sealing together small pieces of apparatus it is unnecessary to employ a side-tube at all. The edges of the tubes are well heated and pressed together, and the junction is melted in the blowpipe flame. The increase of pressure in the apparatus is sufficient to expand the glass, but it requires some practice to carry the operation out effectively.

To connect pieces of apparatus at a distance, a piece of glass tube is cut to the exact length, and connected with one of the leading tubes by a piece of rubber tube about 2 cm. long. The tube is then held in position in a clamp, while the free edges are sealed, and when this is done, the rubber tube is removed and the second junction is made. If the tubes to be sealed *in situ* are of different diameter the larger tube must be heated, drawn out to a long taper, and cut at the right point. This cannot be done in the case of tubes which differ very greatly in diameter.

*India-rubber connections.*—In certain cases where it is impossible to seal the tubes together, rubber connecting tubes may be employed, and, if proper precautions are taken, there is no objection to their use. To connect tubes up to 4 mm. in diameter, thick-walled rubber tubes of about 2 mm. internal diameter and 6 mm. external diameter should be used. The ends of the glass tubes should be rounded in the blowpipe flame and

forced into a piece of the rubber tube about 3 cm. long till they meet. A *single* turn of copper wire rather less than 1 mm. in thickness is brought round each end of the rubber tube, and is twisted tight by means of a pair of pincers.

To render the junction more secure a little tap grease (p. 24) may be run in between the rubber and the glass by means of a heated iron spatula. It is not advisable to heat the ends of the glass tubes before forcing them into the rubber tube; the junction is not rendered much more secure and the interior of the apparatus is filled with the vapour of the decomposed rubber. The junction may be enclosed in mercury in order to render it more thoroughly air-tight (p. 70), it is, however, questionable whether or not gases can pass between the surfaces of the

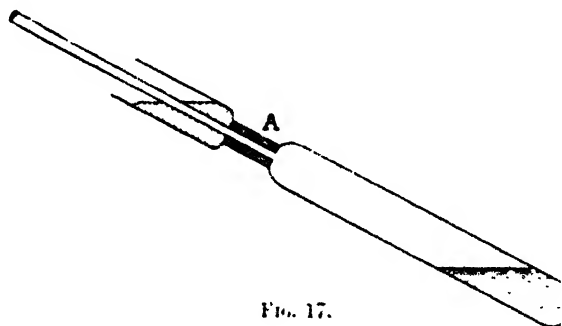


FIG. 17.

mercury and of glass in contact. Both Crookes and Morley state that in order to render a rubber junction, which leaks slowly in contact with air, perfectly air-tight, it should be protected by mercury, and the surface of the mercury should be covered by a layer of sulphuric acid.

To connect pieces of quill tube to tubes of larger diameter the following method has been found convenient (*Proc. R. S.* 60, 442). The larger tube (Fig. 17), which may be of hard or soft glass, is drawn to a neck at A; a piece of thick-walled rubber tube is passed over the end of the small tube, which is then forced into the neck of the large tube. The space above the junction may be filled with mercury or other liquid. This form of connection possesses the advantage that only a very small area of the rubber is exposed to the action of gases inside the apparatus.

*Ground-glass junctions.*—If it is necessary to take a piece of

apparatus apart frequently, it is convenient to make the connections by means of ground-glass junctions.

The usual form of ground-glass junctions are shown in Fig. 18; they may be of any diameter, but the type B is more applicable to larger tubes if the apparatus is to hold a vacuum. The connection consists of a plug and socket carefully ground to fit one another. In A the tubes are of the same diameter. In B the socket is turned out to form a cup, which can be filled with mercury or other liquid to guard against leakage; the liquid can be removed by means of a pipette, made like a small wash-bottle, before the tubes are dis-

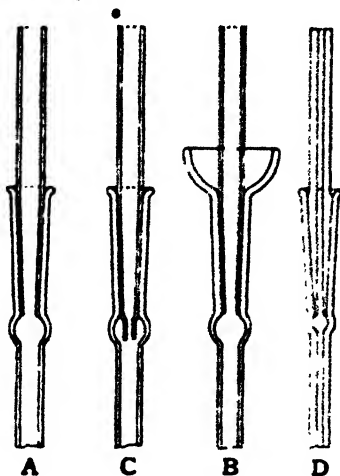


FIG. 18.

connected. The type C was employed by Morley (p. 130) to connect his density-bulbs to the apparatus for filling them. The

plug was sealed to the bulb, and the small projecting tube prevented any of the lubricant, which was used to make the joint tight, from being carried down inside the tube. It is practically impossible to make a junction between capillary tubes without blowing a small bulb to receive the point of the plug, as in Fig. 18, D. Ground-glass junctions of the form shown in Fig. 19 are sometimes employed; they are, however, somewhat difficult to make.

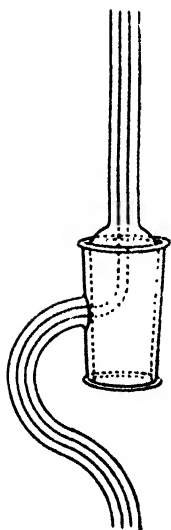


FIG. 19.

*India-rubber cement*, or marine glue, can be used to make very efficient junctions. The cement should be heated *in situ* by a small gas jet.

*Flexible junctions.*—Tubes of lead or steel, or long spirally wound glass tubes, may be used as flexible junctions. Fine steel tubes, such as are used by surgical instrument makers, are the most convenient, and will stand very high pressures.

*Connections between metal and glass.*—The difficulty of joining metal to glass lies in the great difference between the thermal

expansions of the two substances. Metal and glass tubes may be connected by means of elastic cement, the metal being furnished with a socket into which the glass tube fits.

A fusible alloy (Rawson, *Soc. Chem. Ind.*, 1890, 151) which has the same coefficient of expansion as glass has been used, but the junctions are not of a very satisfactory nature, and are only gas-tight when covered with a layer of cement. The composition of the alloy is as follows:—

Bismuth . . .	40 per cent	Antimony . . .	10 per cent
Lead . . .	25 "	Cadmium . . .	10 "
Mercury . . .			15 per cent

The most satisfactory method of connecting glass and metal apparatus is the one first used by Callendar. The metal tube is soldered (Fig. 20) to a narrow platinum tube, which is in turn sealed to the end of a glass tube (p. 298).



FIG. 20.

The platinum tube may be solid drawn, or may be made from a piece of platinum foil rolled on a wire and soldered along the edge with pure gold.

Kammerlingh Onnes employs a steel cap to connect fine steel tubes to the capillary glass tubes of his high-pressure manometer. The steel tube is soldered

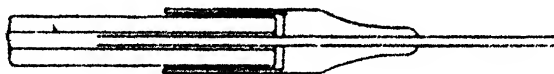


FIG. 21.

through the cap, and passes well within the glass tube. The joint is made with marine glue, so that the solder is protected from the action of mercury which may enter the apparatus (p. 163).

**Stopcocks.**—Modern methods for the manipulation of gases usually involve the use of apparatus, of which glass stopcocks form an important part.

If a stopcock is properly constructed and lubricated with a suitable grease there is no danger of leakage, even when the differences of pressure inside and outside the apparatus is considerable; indeed, it should be possible for a piece of apparatus connected with several stopcocks to remain exhausted for weeks at a time. Glass stopcocks cannot, however, be expected to resist any considerable internal pressure.

The simple glass stopcock in which the leads consist of

two pieces of glass tube of 3 to 4 mm. diameter is too well known to require description. If well made it may be used with safety, but it is usually found that in grinding in the plug a ring is formed at the level of the openings in the barrel, and leakage may occur from one side to the other. Taps in which the leading tubes are of narrow bore, 1 mm. at the most, are more to be recommended as less liable to leakage in this

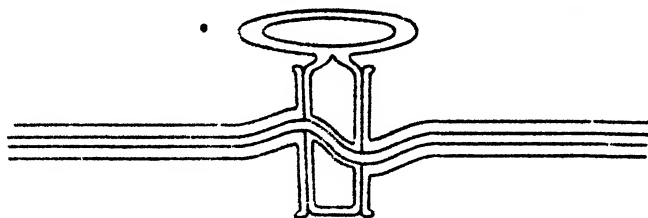


FIG. 22.

direction, and are more largely used in the construction of gas apparatus.

In order to eliminate danger from leakage round the plug, stopcocks are now made in which the leading tubes enter the barrel at points which are not exactly opposite to one another (Fig. 22). The plug is, of course, bored diagonally to coincide

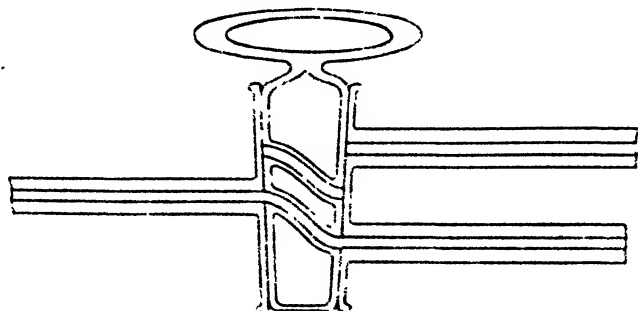


FIG. 23.

with those openings. These stopcocks are to be recommended for accurate work.

*Three-way stopcocks* are of two kinds: those in which the three leading tubes lie in the same plane and at right angles to one another, and in which the plug is pierced in the form of a T; and those in which the leading tubes lie in the plane which contains the axis of the barrel, and in which the plug is pierced by two diagonal holes (Fig. 23).

Stopcocks of the first kind are not to be recommended, but they possess the advantage that the three leading tubes can be placed in communication at the same time. The second form of tap, which was first made by Greiner and Friedrichs, is now in general use. The holes in the plug, which should be about 1.5 cm. in diameter, should be at right angles to one another.

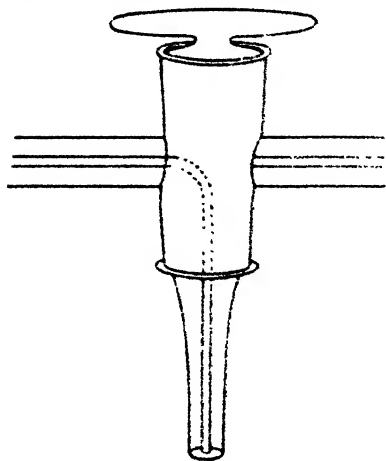


FIG. 24.

A third form of three-way stopcock is sometimes employed (Fig. 24). It is not, however, to be recommended.

*Four-way stopcocks* are sometimes used, and have been found to work in a very satisfactory manner. Since, however, a two-way and a single stopcock can be used for the same purpose, nothing is to be gained by their use.

Stopcocks of steel or of platinum have been used in connection with glass apparatus. The stopcocks are constructed with sockets into which the ends of the glass tubes are cemented (p. 22).

It may be noted that the efficiency of a stopcock does not necessarily depend upon its size but rather on the shape of the plug. Long and narrow plugs cannot be accurately ground to fit the barrel, but are liable to fit badly at the ends. If the plug of a stopcock is 3 cm. long, it should be at least 1.5 cm. in diameter.

Stopcocks which are only in use for a short time may be lubricated with tallow or other grease, but if it is necessary to employ them over a considerable period without relubrication they are liable to become jammed owing to the grease working out at the ends. A very efficient lubricant, which does not deteriorate on keeping, and which, owing to its viscous nature, does not work out at the ends of the plug, and which possesses the additional advantage that it gives off no hydrocarbon vapour, may be made in the following manner.

Two parts of soft rubber clippings, one part of vaseline, and one-eighth part of hard paraffin wax are heated together in a basin on a sand-bath. The mixture is thoroughly stirred till the rubber

is completely dissolved, and then allowed to cool. The product should be a soft, black, and somewhat sticky substance; it should be entirely without odour. The lubricant should be kept in a closed wide-mouthed bottle.

In lubricating a stopcock the plug and barrel should be thoroughly cleaned, and a little of the grease rubbed over the plug with the finger. After the plug has been turned in the barrel several times the tap should appear perfectly transparent and free from streaks.

The use of a rubber lubricant is of course restricted to experiments which do not involve the use of corrosive gases or liquids. In the latter case it is better to employ metaphosphoric acid as a lubricant. The stopcock is very carefully cleaned, and the dry plug is dipped into pentoxide of phosphorus. On exposure to air, water is absorbed and metaphosphoric acid is produced.

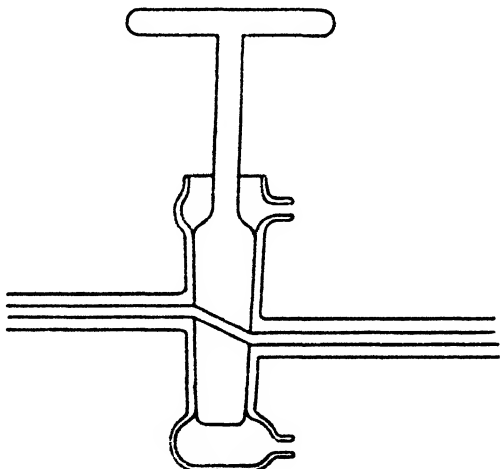


FIG. 25.

Since metaphosphoric acid is not a very efficient lubricant it is sometimes necessary to take additional precautions against leakage by protecting the ends of the plug by mercury cups. The form of tap usually employed is shown in Fig. 25.

An ingenious method has been employed by Dr. Morley in order to temporarily close glass vessels without using a stopcock.

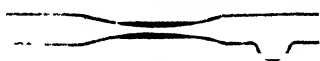


FIG. 26.

The glass tube is drawn out as in Fig. 26, and a small bulb is blown at the side close to the narrow portion. A small quantity of fusible metal is placed in this bulb, and in order to close the apparatus this is melted by gently warming and allowed to flow into the narrow portion of the tube, where it solidifies.



## CHAPTER IV

### GAS-MANIPULATION : COLLECTING AND STORING GASES

Gas-tubes and mercury-troughs. Collecting gases delivered by the mercury-pump.

The syphon pipette—Gas-holders and gasometers. Storing and transporting samples of gas—Collecting gases from natural waters, etc. Gases evolved during chemical reactions.

THE method of removing a gas from any piece of apparatus by means of the mercury-pump has already been referred to. When a Töpler or Sprengel pump is employed the gas can be collected without loss or risk of contamination in a tube previously filled with mercury, and inverted in the trough over the upturned end of the capillary delivery tube of the pump (p. 9).

*Gas-tubes and mercury-troughs.*—The tubes which are used for collecting and storing gases may be of any size, but the dimensions are limited by the internal diameter of the mercury-troughs in use, and by the lengths of the syphons on the pieces of apparatus into which the gas is to be transferred, a length of 12 cms. and diameter of about 2.5 cms., giving a working capacity of 50 cubic centimetres, will be found convenient. The tubes should be contracted at their open ends as in the figure, so that they can stand in small porcelain crucibles, or may be closed by the finger.



FIG. 27.

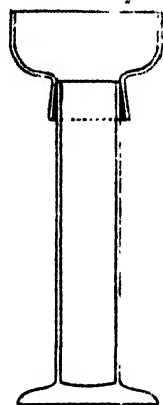


FIG. 28.

In order to economise mercury it is convenient to use a trough of the form shown in Fig. 28. The trough should be about 10 cm. wide at the top, but the lower portion need only be about 7 mm. wider than the gas-tubes in use: a little extra space is, however,

more convenient. These troughs are somewhat difficult to obtain, but they may easily be made by cementing the top of a wide-mouthed bottle on to a gas jar as in the figure.<sup>1</sup>

The gas-tubes may be filled with mercury so as to leave the glass free from air-bubbles in the following manner. A piece of glass tube, of about 1.5 mm. internal diameter, is bent into a syphon of which the shorter limb, which is somewhat longer than the gas-tube, is drawn to a point. The short limb of the syphon is passed into the tube, which is pressed mouth downwards below the surface of the mercury in the trough. When all the air has escaped from the tube it is allowed to rise, and the syphon, which

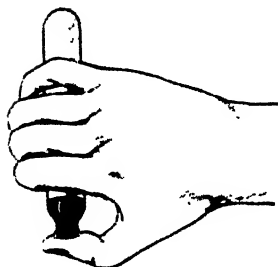


FIG. 29.



FIG. 30.

is still held below the surface of the mercury, is removed from beneath it.

A gas-tube containing gas or mercury may be transferred from one trough to another by merely closing it with the finger (Fig. 29); the following method is, however, preferable. A porcelain crucible, about 2 cm. in diameter, is brought below the mouth of the tube which may then be lifted from the trough (Fig. 30). Samples of gas may be preserved over mercury in this way for any length of time, the tubes standing in a rack made by screwing strips of brass to a board at the back of a shelf, and bending them so that they lightly grip the tube.

<sup>1</sup> To cut a bottle or large cylinder of glass a piece of machine-cut paper is first wrapped round the glass, and a circular cut is made with a file or glass-knife along its edge. Two strips of wet folded filter-paper are then passed round the cylinder, one on each side of the cut, and a fine blowpipe flame is directed on to the glass between them while the cylinder is slowly rotated. A piece of iron wire 5 mm. in thickness, bent into a semicircle of the same diameter as the cylinder, if heated and applied to the glass will cause it to crack along the line of a file-mark. The rough edges of the glass may subsequently be removed by means of a file.

The *syphon pipette* (Fig. 31) is usually employed for removing the gas from a tube. The body of the instrument may be of any size, and may be graduated for the measurement of volume. The syphon should be of millimetre bore tube of uniform diameter.

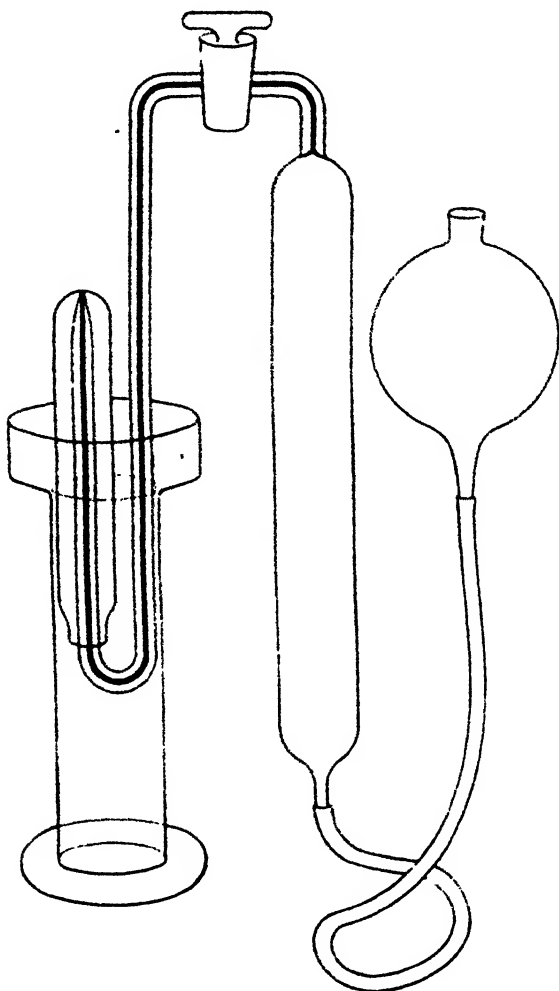


FIG. 31.

The reservoir should be connected with the pipette by means of a piece of rubber pressure tube, and the joints should be wired. The apparatus is usually held in a clamp, and the mercury-trough is adjusted to a convenient height on blocks of wood.

The apparatus is first filled with mercury, and the reservoir is lowered and raised again two or three times to get rid of air-bubbles. The tube containing the gas is then brought over the syphon, by raising the trough if necessary, the reservoir is lowered, the tap is turned, and the gas is taken into the pipette. Sufficient mercury should be drawn over with the gas to completely fill the capillary tube.

The syphon may also be applied to larger mercury gasholders; those of the type shown in Fig. 32 are made to contain about 250 c.c.

It is sometimes convenient to deliver gases directly from the pump into a gasholder, particularly if the quantity of gas is large. The vessel *a*, which is connected with the gasholder *b* by a capillary

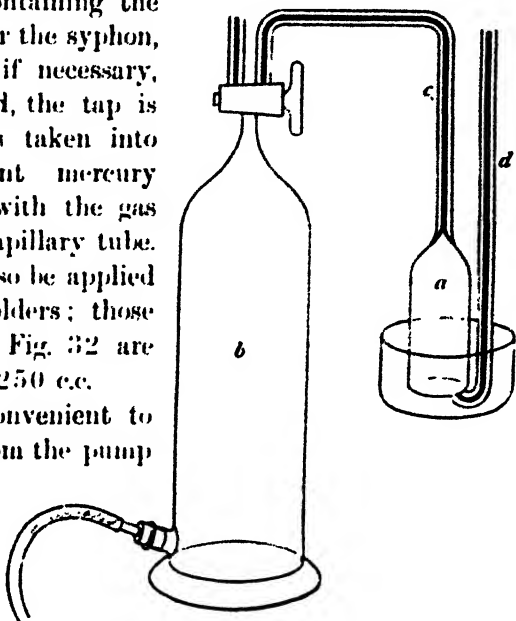


FIG. 32.

tube *c*, stands in a mercury-trough directly over the upturned end of the delivery tube *d* of the pump: the tube *c* should not, of course, be carried to any great vertical height. If the reservoir attached to the gasholder is so placed that the mercury in it lies below the level of the mercury in the trough, it will merely be necessary to turn the tap from time to time in order to remove the gas from *a*.

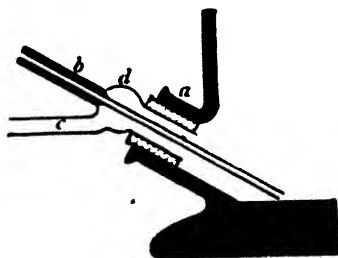


FIG. 33.

The glass fitting *bed* is inserted into the lower opening *a* of the gasholder through a rubber stopper. The gas is delivered

*Collecting gas over potash.*—It is often convenient to collect a gas over potash or other liquid reagent in order to remove one of its constituents in a single operation. One of the larger gasholders (Fig. 32) may be adapted for this purpose by means of the arrangement shown in Fig. 33.

through the tube *b* which passes below a layer of mercury covering the bottom of the gasholder, the potash escapes through *c*

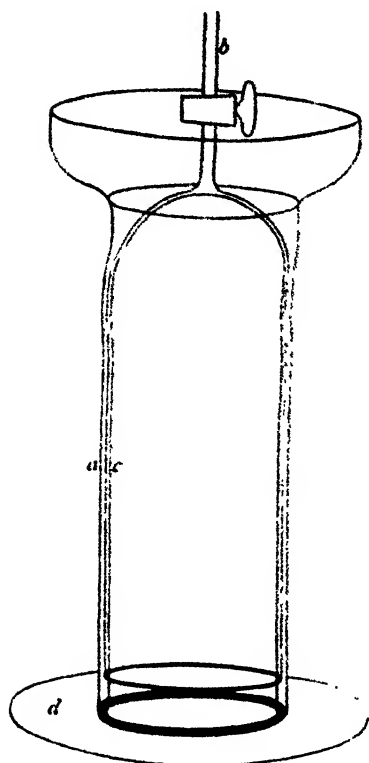


FIG. 34.

which is connected with a reservoir; the apparatus is similar to that employed in nitrogen determinations.

*Gasometers* are sometimes employed for storing gas, but they are somewhat difficult to manipulate. The form shown in Fig. 34 possesses the advantage that it does not require much mercury. Concentric rings are turned in a block of hard wood *d*, and two concentric cylinders *a* and *c* are cemented into them; the gasholder *b* fits closely over the inner cylinder. In using the instrument the mercury must first be drawn up into the stopcock, and on account of the buoyancy of the glass, pressure must be exerted to expel the gas.

Gasometers of a similar form, holding from 20 to 200 litres, were employed by Professor Ramsay and the author in the preparation of argon on a large scale. The smaller ones were of zinc, and the annular space, which contained water, was about 2 cm. wide; a section of one of them is shown in Fig. 72. The pressure was adjusted by hanging weights on to the string which was attached to the top of the gasometer and passed over the pulleys, or by placing weights on top of the gasholder. The top of the gasometer and inside cylinder were made dome-shaped in order to allow of the gas being completely expelled.

*Tubulated bottles* of the form shown in Fig. 35 may be conveniently used as gasholders. As the gas enters through the stopcock *a*, the water is expelled into a second vessel through a rubber tube connected with the opening *b*.

*Storage of samples of gas.*—For the safe keeping of samples of gas it is advisable to seal them up in glass tubes so arranged

that the gas can be easily removed without loss or contamination. The tube which is to contain the gas should be drawn out at either end as in Fig. 36; its capacity should be somewhat greater than the volume of the gas under normal temperature and pressure. The capillary portion *a* of the tube should be about 1 cm. in length; the tube should be slightly contracted at *b* and *c* to hold the

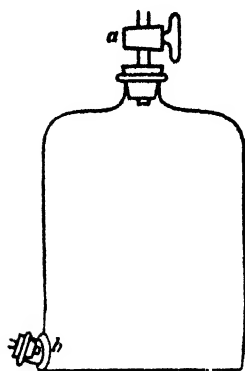


FIG. 35.

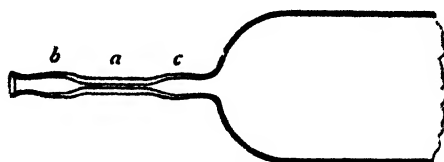


FIG. 36.

rubber tubes which are attached in introducing and withdrawing the gas. The gas may be introduced from a syphon gas-pipette by one of the following methods.

The tube is held in a vertical position in a clamp so that the upper end of it lies close to the stopcock on the gasholder. Two rubber tubes are then attached; a long one to the lower end leading to a mercury reservoir, and to the upper end a tube of sufficient length to make the connection with the gasholder. It is advisable to hold a short section of the long rubber tube in a clamp, as the strain caused by the weight of the mercury in it may break the capillary glass tube to which it is attached.

Mercury is then poured into the reservoir till it fills the glass tube and rises into the rubber tube at the top of it, completely expelling all the air. The lower rubber tube is then closed by means of a screw clamp, and the short rubber tube is slipped over the tube leading to the stopcock on the gasholder, taking care that no air is enclosed; the junction is made secure with wire. By opening the stopcock on the gasholder, loosening the screw clamp, and lowering the reservoir, the gas is allowed to flow into the glass tube and replace the mercury. If the tube is of the right size when the mercury is at *b* (Fig. 36) at both ends of the glass tube, the gas will be at slightly reduced pressure, and the capillary portion of the tube can be heated in a blowpipe flame and sealed off with safety.

Instead of filling the tube with mercury it may be attached

by one end to the gasholder, and by the other to the pump. The air is removed by exhaustion, the tube is sealed from the pump, and the gas is introduced in the manner already described.

The gas may be either expelled from the tube by means of mercury, or drawn off through the pump; the second method is the more convenient. A piece of rubber tube is slipped over the end of the glass tube (Fig. 36), which has been previously scratched with a file, and secured by means of a turn of wire; the other end is attached to the pump. After the air has been removed from the leading tubes the point of the glass tube which is inside the rubber tube is broken, and the contents of the tube are pumped off and collected. If the end of the glass tube nearly fills the rubber tube, so as to render the exhaustion slow, the tube may be compressed by means of a screw clamp, so as to make it somewhat oval in section.

The only difficulty involved in expelling the gas from the storage-tube with mercury lies in attaching the tube connecting it with the reservoir and gasholder, which are previously filled with mercury, without introducing air. The operations are practically the same as those involved in filling the tube by the method first described.

Storage-tubes with glass taps at either end may be used for conveying samples of gas from one place to another for analysis.

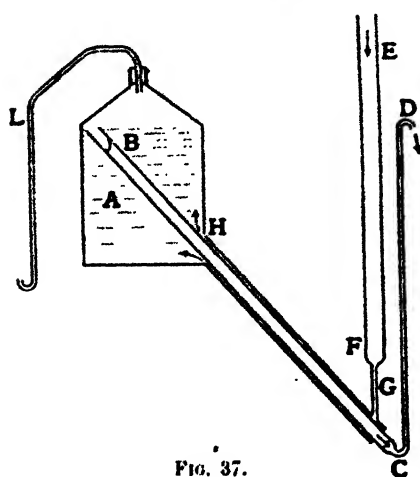


FIG. 37.

The taps should be well ground and lubricated, and of capillary bore.

*Gases from natural waters and mineral springs.*—Lord Rayleigh has described an apparatus by means of which it is possible to obtain the gas from a large quantity of water. "The boiler A was constructed from an oil-can, and was heated by an ordinary ring Bunsen burner. For the supply and removal of water two co-axial tubes of thin brass, more than 4 feet in length, were applied on the regenerative principle.

The outgoing water flowed in the inner tube, BC, from C to D by prolongation of composition tubing. The inflow water was delivered into a glass tube at E, passed through the brass connecting tube FG into the narrow annular space between the two principal tubes, GH. The neck of the can was fitted with a rubber cork and delivery tube, L, by means of which the gases were collected over water in the ordinary way" (*Phil. Trans.*, 1895, 226).

In actual working\* it is necessary to keep the water boiling very steadily, by carefully protecting the burner from draughts. The temperature of the water in the basin in which the gas is collected should also be kept down to about 70° by means of a coil of composition tube through which cold water is circulated.

The delivery tube may be connected directly with a gasholder (Fig. 35) through a stopcock. A condenser about 40 cm. long, with an inner tube of narrow bore, is interposed in order to condense the steam. The gas is carried along the tube between the pellets of water which are formed.

Lord Rayleigh examined the gases from a large number of natural waters, and the method has also been employed by Ramsay and Travers (*Proc. Roy. Soc.*, 1897, 60, 442).

For the quantitative estimation of the gases dissolved in water the water must be introduced into a vessel previously exhausted, and in communication with a pump, and boiled. A convenient apparatus for the purpose has been described by Trumann (*Chem. Soc. J.*, 1894, 96).

The flask is connected by means of a rubber stopper with a bulb, which serves as a condenser. The stem of the bulb passes down to the bottom of the flask, and a hole is made in it for the passage of the steam. The neck of the bulb is sealed to two tubes, one leading to a graduated funnel, the other through a stopcock to the pump. A ring of composition tube pierced with holes surrounds the tube above the bulb; it is connected with the water supply, and serves to maintain a current of water over the surface of the bulb. The water runs into a catch-water below the bulb, and is conducted away. A similar apparatus is described on p. 112.

In many cases gases are given off with the water in mineral springs. In some cases the gases consist chiefly of carbon dioxide, in others, particularly when sulphides are present, of nitrogen, often



containing rather more argon than is present in atmospheric nitrogen, and sometimes helium.

The gas may be often directly collected by inverting a bottle filled with water over an ordinary funnel immersed in the spring: the bubbles of gas rise into the funnel, and so into the bottle. The bottle is subsequently stoppered below the surface of the liquid, and the neck is afterwards secured with sealing-wax. To remove the gas the bottle is immersed in a trough of water, and the gas is drawn out by means of a glass siphon into a suitable gas-holder.

Very often, on account of the temperature of the water, or for other reasons, it is quite impossible to collect the gas in this manner. For the examination of the gases from the springs of Cauterets (Pyrenees) the following method was employed (*Proc. Roy. Soc.* **60**, 442). Vessels made of stout sheet-tin A, with taps at either end, were used to collect the gas. A piece of rubber tube B was attached to one of the taps, and the tin was filled with water from the spring. A tin funnel D at the end of a long piece of rubber tube C was then lowered into the spring, and water was drawn up into the tube which was attached to the second tap. The tin was then fixed in a vertical position, and when the funnel was brought over points from which

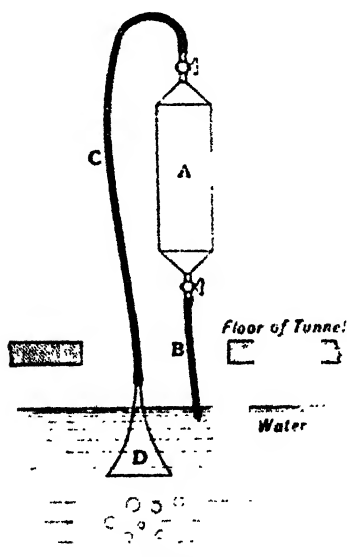


FIG. 38.

the gas was issuing the gas rose through the tube into the tin, replacing the water, which flowed back into the well (Fig. 38).

*Gases evolved during sealed-tube reactions.*— In studying the gaseous constituents of mineral substances it was found necessary to heat the finely powdered minerals in sealed tubes with sulphuric acid to a high temperature in order to completely decompose them (*Proc. Roy. Soc.* **64**, 132). The acid was poured into the bottom of a thick-walled tube, and the mineral was weighed out into a tube with a rod sealed to the bottom of it so as to keep it above the surface of the acid. The tube was then drawn out as in

Fig. 39, A, connected with the pump by means of a rubber tube, exhausted, and sealed at the capillary portion.

After heating for a time sufficient for the complete decomposition of the mineral, the tube was again attached to the pump, as in Fig. 39, B. After removing the air from the connecting tube the point of the tube, previously marked with a file, was broken inside the rubber tube, and the gas was pumped out and analysed.

*Sampling gases from rooms, etc.*—The samples of gas may be taken in tubes of the form described on p. 31. A good current of the gas may be drawn through the tube by means of an aspirator; Hempel suggests using a small rubber hand-pump. A number of samples may be taken in gas tubes in the following manner. A current of gas is made to pass along a tube by means of an aspirator or water-pump. A syphon pipette with a two-way stopcock is connected with the tube so that from time to time samples may be drawn off and transferred to tubes. The tubes may be placed on one side in crucibles, and the samples subsequently analysed.

*Sampling of furnace gases.*—This question has been so fully dealt with in several works on technical gas analysis that it will only be necessary to touch lightly upon it here. The use of unprotected tubes of either iron, porcelain, or platinum is open to objections, for, in the first case, the chemical composition of the gases may be affected, and it is known that both porcelain and platinum, when hot, readily admit of the passage of hydrogen. Winckler's plan of introducing a double-walled tube of the *tuyère* form, through which a current of water circulates, is probably the best (*Anleitung zur chemischen Untersuchung der Industrie-gase*).

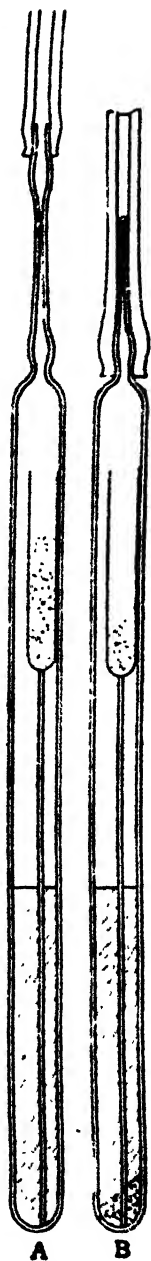


FIG. 39.

## CHAPTER V.

### THE PREPARATION OF PURE GASES

Apparatus employed in the production of gases :—Gases evolved during sealed-tube reactions—Apparatus employed in the purification of gases :—Reagents, pentoxide of phosphorus, etc.—Hydrogen :—Oxygen :—Electrolysis :—Chlorine :—Fluorine :—Nitrogen :—Carbon dioxide :—Carbon monoxide :—Nitrous oxide :—Nitric oxide :—Ammonia :—Phosphoretted hydrogen :—The halogen acids :—Sulphur dioxide :—Sulphuretted hydrogen :—Ethane :—Methane :—Acetylene :—Ethylene.

In selecting a method for the production of a gas it is necessary to take into consideration the following points :—

1. It must be possible to completely remove all air from the apparatus either by exhaustion or by means of a current of the gas.

2. The gas, when first generated, should be so pure as to need little purification. If this is impossible, a method should be selected with regard rather to ease with which the impurities can be removed, than to the quantity in which they are generated ; it would be easier to remove a large quantity of carbon dioxide than a trace of hydrogen from most gases.

Chemical substances, whether elementary or compound, may be obtained by processes which fall under one of three headings :—

(1) Electrolysis.

(2) The action of heat on another substance.

(3) The interaction of two or more substances.

(1) *Electrolytic methods* are only applicable to the preparation of a few gases, such as oxygen, hydrogen, and ethane. The method is rarely used.

(2) *By the action of heat upon solid substances.*—The substance may be heated in a hard glass tube connected either directly to the pump, or through tubes containing chemical re-

agents. The connection may be made by means of a piece of rubber tube or by means of a ground-glass junction.

If the quantity of gas is not large it may be pumped off as generated (see p. 9), and delivered into a collecting tube; but if a large quantity of gas is given off, the following method will be found more convenient. A syphon tube of small internal diameter is connected at right angles with the tube connecting the apparatus in which the gas is generated with the pump (Fig. 40). The long limb *a* is bent upward at its lower end, and dips into a basin of mercury. When the apparatus is exhausted the mercury rises to *b*, but when, after closing the stopcock, the substance in *c* is heated, and the pressure in the apparatus rises, the gas escapes through the mercury in the basin, and may be collected in tubes. The residual gas may be removed by means of the pump. I shall refer to this piece of apparatus as the syphon delivery tube.

(3) *By the action of a liquid on a solid substance.*—The solid

is introduced into a flask (Fig. 41), which has a tap funnel

sealed to the side of it, and which may either be hermetically sealed or closed with a rubber or glass stopper; it is connected with the syphon delivery tube and to the pump.

When exhaustion is nearly complete a little of the liquid is allowed to pass the stopcock in order to make sure that no air is present in the bore. After complete exhaustion the liquid is admitted carefully so as to avoid frothing, heat being applied if necessary.

*By the interaction of two liquids or of two substances in solution.*—The liquids are admitted either separately or together through the tap funnel; no particular precautions beyond those already mentioned need be observed.

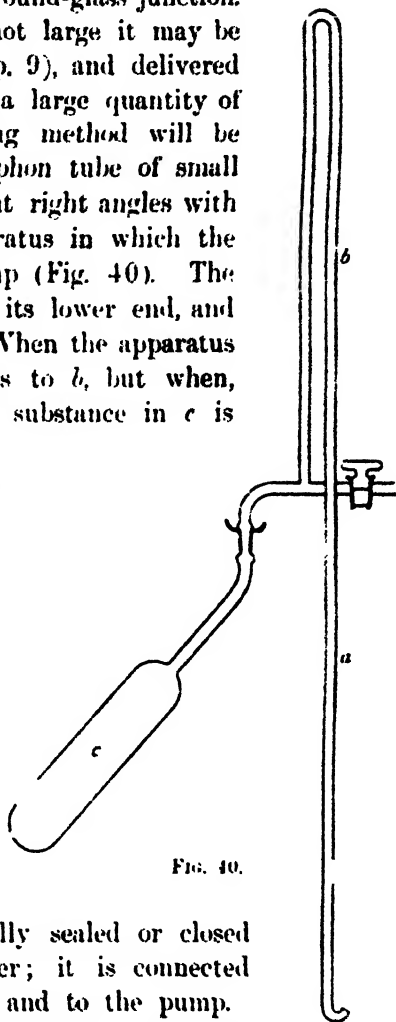


FIG. 40.

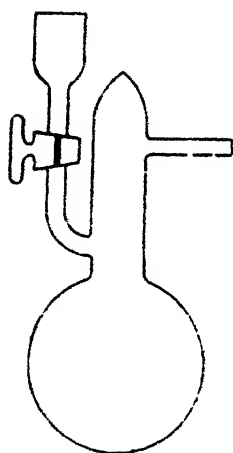


FIG. 41.

*Tube furnace.*—For heating long glass tubes the ordinary form of combustion furnace is conveniently employed. These furnaces are, however, too large for most of the operations with which we are concerned, and to meet the requirements of the work, Professor Ramsay has designed an attachment to the Bunsen burner for heating glass tubes up to 8 inches in length (Fig. 42).

The attachment fits on to the top of a  $\frac{5}{8}$  inch burner, so that it can easily be removed. The gas issues from a slit along the top of the horizontal portion, and the slit can be closed by means of four split tubes *c, c'*. The two end pieces *d, d'* support a brass trough in which the tube lies; the trough may be lined with asbestos, but this is usually unnecessary.

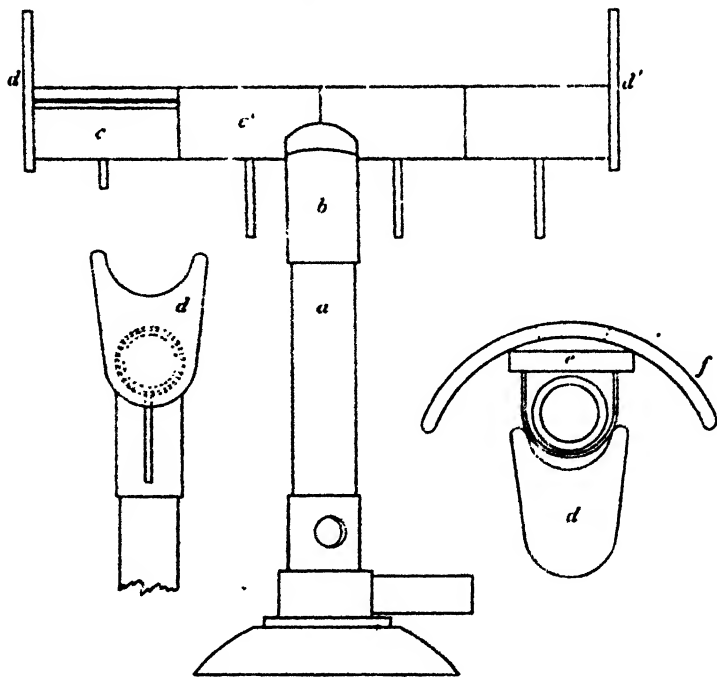


FIG. 42.

If it is necessary to heat the tube to redness, an asbestos

hood *f* is supported above it by means of a piece of fire-clay tile *e* placed at each end. The hood is made of a strip of asbestos cardboard 8 inches long by 3 inches wide pierced down the middle line by a number of holes; the holes may be cut with a cork-borer.

*The removal of impurities from a gas* in the course of preparation is usually accomplished by bringing it into intimate contact with one or more substances which absorb the impurity without at the same time giving off any gas or vapour which cannot be easily removed. The apparatus should be so arranged that the reagent presents a considerable surface to the gas, which should not pass over it at a high velocity or at reduced pressure.

If a gas is passed directly from the generating vessel through the purifying tubes to the pump, it will not be as pure as if it had been allowed to escape at full pressure. Helium generated by heating clévite in a tube, and passed directly over red-hot copper oxide to the pump, will still contain hydrogen, even if the tube containing the copper oxide is of a considerable length. In order to obviate this difficulty the syphon delivery tube (p. 37) may be employed.

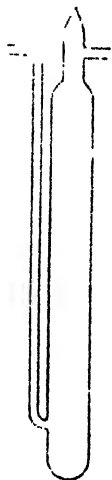


FIG. 41.

U-tubes may be conveniently employed to hold solid reagents or liquid reagents in contact with pumice or some other absorbent. If the apparatus is to be exhausted, the tubes should be made without stoppers, and should be sealed after they are filled with the reagent. A U-tube with one limb sealed is shown in Fig. 43.

Tubes of the type shown in Fig. 44 may be used to contain reagents in the same way.

Four common forms of tubes to contain purifying reagents are shown in Fig. 45. The types *a*, *c*, and *d* may be used for liquid reagents, and are particularly useful in cases where, during a chemical reaction, a quantity of water vapour is given off and must be absorbed. The tubes *c* and *d* may also be used



FIG. 43.

for solid reagents, such as phosphorus pentoxide, which can be introduced through the stoppered openings. The tube *b* is the

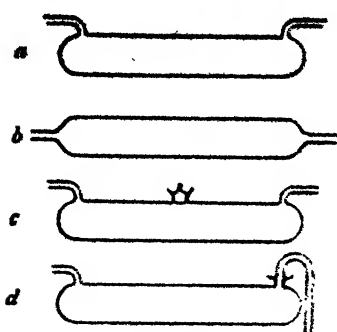


FIG. 45.

simplest and most convenient form that can be employed with solid reagents. A piece of glass tube 2.5 cm. in diameter is sealed at one end to a piece of quill tube, leaving the other end open. A plug of glass wool is placed in the bottom of the tube, which is then filled with the reagent to within 4 cm. of the top. A second plug of glass wool is pressed down on top of the reagent, and

the tube, after being carefully cleaned with a wet and a dry cloth, is drawn out in the blowpipe flame, and sealed to a second piece of quill tube. When phosphorus pentoxide is employed the tube when in use must lie in a horizontal position, or it will become partially or completely clogged by the semi-fluid metaphosphoric acid.

Wash-bottles are rarely employed in cases where it is necessary to exhaust the apparatus. A wash-bottle with a bye-pass (Fig. 46), is, however, sometimes convenient.

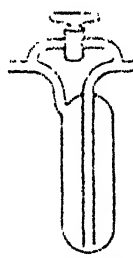


FIG. 46.

In certain cases it is impossible to exhaust the apparatus in which the gas is generated. Special precaution must then be taken to secure the

complete removal of the air from the apparatus by the escaping gas, and in constructing the apparatus care must be taken to keep the internal volume small

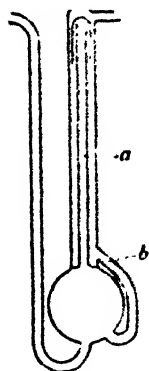


FIG. 47.

without reducing the surface of the purifying agents exposed to the gas. Dead ends and blind channels must be avoided or made as short as possible. If the gas is generated by heating a substance, heat must first be applied to the extremity of the tube containing it.

*The Richardson wash-bottle.* In this apparatus (Fig. 47) the gas is introduced at the bottom of the bulb, and rises in bubbles through the tube *a*, carrying liquid with it; the liquid returns to the bulb through the tube *b*. There is very little free space above the surface of

the liquid, and the gas is thoroughly exposed to the action of the reagent.

*The Pettenkofer absorption tube* (Fig. 48).—The gas is introduced through a jet at the bottom of a long inclined tube, which is nearly filled with the reagent. It passes in bubbles along the upper surface, and escapes at the open end. In a more compact form of the apparatus the inclined tube is wound into a spiral, which may be of considerable length.



FIG. 48.

Neither of these pieces of apparatus should be used if there is any danger of liquid being sucked back into the generating vessel. In this case the reagents should be contained in U-tubes.

The gas should be allowed to escape freely from the apparatus before any of it is collected. The tube from which the gas escapes should pass beneath the surface of mercury.

*The method of purifying gases by liquefaction and fractional distillation* is dealt with in Chapter XVI.

*Phosphorus pentoxide*.—This reagent is almost universally used as a dehydrating reagent in working with gases, but it is somewhat difficult to obtain pure. The oxide should be perfectly white and quite free from discoloured nodules and sticky masses of metaphosphoric acid. When exposed to the air it should deliquesce without turning red or giving off any odour. The principal impurities consist of the lower oxides of phosphorus, some of which are in themselves volatile and react with gases, such as chlorine and ozone, and with water vapour to yield phosphoretted hydrogen.

In order to oxidise the lower oxides Threlfall (*Phil. Mag.*, January 1893) volatilised the crude pentoxide over platinised asbestos in a current of oxygen. Shenstone and Beck (*Chem. Soc. Jour.*, 1893, **63**, 475) found that the platinum quickly became covered with a layer of phosphide and so rendered useless: they recommend the use of platinum sponge. The pentoxide can be obtained almost entirely free from the lower oxides by throwing it into a red-hot porcelain basin, and stirring it in a current of oxygen.



*Hydrogen, H<sub>2</sub>.*—(a) Moderately pure hydrogen may be obtained by the action of dilute sulphuric acid upon zinc which has previously been platinised. The ordinary Kipp's apparatus may be conveniently used, and to guard against absorption of air by the acid the open bulb may be connected with a reservoir containing hydrogen confined over water.

Hydrogen should not be passed through a solution of potassium permanganate; for although this reagent completely removes arsenuretted hydrogen, it gives rise to traces of oxygen in the gas.

(b) Very pure hydrogen may be obtained by the action of caustic potash upon aluminium. The metal should, however, be free from carbon, which may be present to a certain extent in the metal, and give rise to the formation of hydrocarbons.

(c) Metallic sodium has the property of absorbing hydrogen at a temperature a little above its melting point, and giving it up again at a higher temperature. If the metal is free from hydrocarbons the gas obtained in this manner is perfectly pure and free from moisture.

Troost and Hautefeuille (*C. r.* 78, 809) have determined the dissociation pressures of sodium hydride at different temperatures.

Temperature.	Pressure.	Temperature.	Pressure.
330°	28 mm.	390	284 mm
340	40 ..	400	447 ..
350	57 ..	410	598 ..
360	75 ..	420	752 ..
370°	100 ..	430°	910 ..
380	150 ..		

The metal begins to absorb hydrogen at about 100°, and when saturated it appears that the product corresponds to the formula Na<sub>2</sub>H.

The metal, which has been carefully freed from impurity, is placed in the upper part A of the apparatus shown in Fig. 49. The tube *a* is connected through a stopcock and a phosphorus pentoxide tube to a Kipp's apparatus generating hydrogen, and the tube *b* to a mercury-pump and to the apparatus which is to receive the gas. After exhausting the apparatus, both A and B are warmed and gently tapped till the sodium flows down into the lower tube. The gas is now admitted, and absorption is allowed to proceed, the temperature of the lower vessel being maintained at about

150°. When the metal is saturated the stopcock on *a* is closed, and the temperature is raised. The gas may now be collected after allowing the first portion to escape.

The sodium may be again saturated with hydrogen, and a second quantity of the pure gas so obtained.

Small quantities of pure hydrogen may most conveniently be obtained by means of metallic palladium: the metal is, however, very expensive. The quantity of hydrogen which 1 gram of palladium will absorb varies considerably with the state of the metal: using palladium sheet, Morley found it to be 0.0063 grams of hydrogen for every gram of the metal. Practically the whole of the hydrogen is evolved *in vacuo* at the ordinary temperature.

The metal, either in strips or in the spongy condition (the pieces of sponge should be well hammered on an anvil to render them compact), is strongly heated in a blow-pipe flame or in a muffle-furnace. While still hot the metal is placed inside a tube fitted with a stopcock, which is then sealed at the other end, attached to a pump, and exhausted. The palladium is then charged with hydrogen by attaching the tube to a Kipp's apparatus, and allowing the absorption to proceed for about an hour; a considerable amount of heat is generated during this process.

In order to obtain the pure hydrogen the palladium tube is attached to a pump, syphon-delivery tube, or apparatus into which the gas is to be introduced. The tube is then gently warmed, and after allowing the first portion to escape, sufficient gas is collected, and the metal is allowed to cool.

Oxygen,  $O_2$ , may be conveniently prepared by heating pure potassium permanganate. Since the gas is evolved at a very low temperature, the tube in which the permanganate is contained may be of soft glass, and may be sealed directly to the tube containing the purifying reagents. Traces of carbon dioxide may be present produced by the oxidation of dust, etc., in the permanganate; the gas may be purified by passage over solid

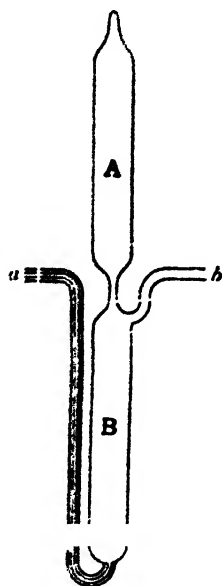


FIG. 49.

potash, and pentoxide of phosphorus. The one objection to this method is the difficulty of getting rid of the oxide of manganese which is carried, either in suspension or in the state of vapour, for a considerable distance through the tubes.

Potassium chlorate should not be employed for the preparation of pure oxygen unless special precautions are taken to purify the gas from traces of chlorine, hydrochloric acid, and ozone, which are invariably found in it. Morley (Smithsonian Institution) passed the gas from potassium chlorate through a red-hot tube containing finely divided silver, and subsequently over a strong solution of caustic potash, over strong sulphuric acid, and through pentoxide of phosphorus (p. 131).

Shenstone suggests the use of a mixture of equal weights of sodium and potassium chlorates, which has a much lower melting-point than either of these compounds by itself.

Oxygen may become ozonised by passage through a Sprengel pump; the quantity of gas which is converted into the active variety is, however, very small.

*Electrolysis of dilute sulphuric acid.*—

This method may be conveniently employed if a constant current of either of the gases is required for a considerable period; it does not, however, conveniently serve for the preparation of small quantities of the gases in a state of purity.

A form of apparatus which may be conveniently employed is shown in Fig. 50. The two vertical tubes A and B, which contain the electrodes, are connected by the horizontal tube C. The tube C is divided by a disc of porous material, cut from a battery cell and cemented in position, in order to check the diffusion of liquid from A into B, and consequent contamination of the hydrogen by dissolved oxygen and *vice versa*. The electrodes are of sheet platinum rolled into a spiral and attached to stout copper leads which do not come into contact with the liquid. The

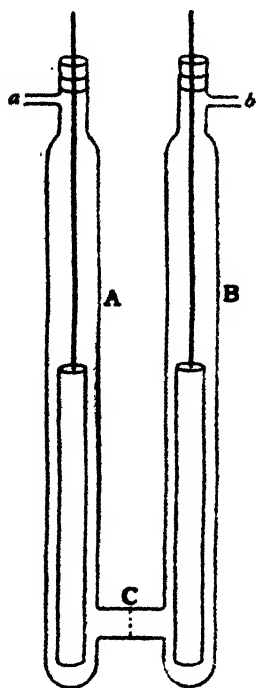


FIG. 50.

leads are cemented through the upper ends of the vertical tubes,

which are made narrow for the purpose; the gases escape by the side-tubes *a* and *b*. The strength of the acid should be about 1 in 6, the current should not exceed 0.1 ampère per sq. cm. of surface. The lower part of the apparatus should stand in a vessel through which cold water is circulated.

In order to obtain a steady current of either of the gases the tube *a* is connected to a vertical tube passing to such a depth below the surface of the water in a vessel, that the pressure in *A* is equal to the pressure in *B*, and there is no flow of liquid across the diaphragm. The side-tube *b* is connected to a hard glass tube containing copper oxide to remove traces of hydrogen if oxygen is being collected, or metallic copper in the case of hydrogen. The gas has then only to be passed through drying reagents. The quantity of oxygen or hydrogen can easily be calculated, since it is known that 1 ampère produces 0.372 gram of hydrogen in one hour.

*Electrolytic gas* can be produced by means of an apparatus containing two electrodes in the same glass tube.

*Fluorine*,  $F_2$ , was obtained in 1886 by M. Moissan by the electrolysis of the compound  $HF.KF$  dissolved in pure hydrofluoric acid in a platinum apparatus.<sup>1</sup> Hydrofluoric acid,  $H_2F_2$ , as it should be written, is itself practically non-conducting, and even in aqueous solution is slightly dissociated; electrolysis of solutions of its salts results in the formation of hydrogen, oxygen, and ozone.

On account of its chemical activity, all experiments on fluorine must be carried out in apparatus of platinum, of platinum-iridium, of fluor-spar, or of some substance which is at first attacked with formation of an insoluble layer of a fluoride. Recently M. Moissan has employed copper vessels in the preparation of fluorine; the platinum-iridium electrodes cannot, however, be dispensed with. It is particularly important, when working with copper vessels, that the hydrofluoric acid should be perfectly anhydrous.

The latest form of M. Moissan's apparatus is shown in Fig. 51. The U-tube *A* which contains the hydrofluoric acid and potassium hydrogen fluoride is of copper or platinum, and has a capacity of about 40 cu. cm. The electrodes *B*, *B'* are rods of platinum-iridium attached at their lower ends to plates of

<sup>1</sup> A full account of his work on the subject has recently been published by him under the title *Le fluor et ses composés*.

the metal bent into cylindrical form. The rods pass through holes in cylinders of fluor-spar which exactly fit the top of the tube, gas-tight junctions being secured by washers of lead which are compressed between the screws at the top of the tube and brass caps which fit over them. The gases, hydrogen and fluorine, produced by the electrolysis escape at the tubes C, C' which can be connected by means of platinum screw-unions with any other piece of apparatus. The U-tube is placed in a bath of methyl chloride (p. 247), supplied from the cylinder D, and boiling

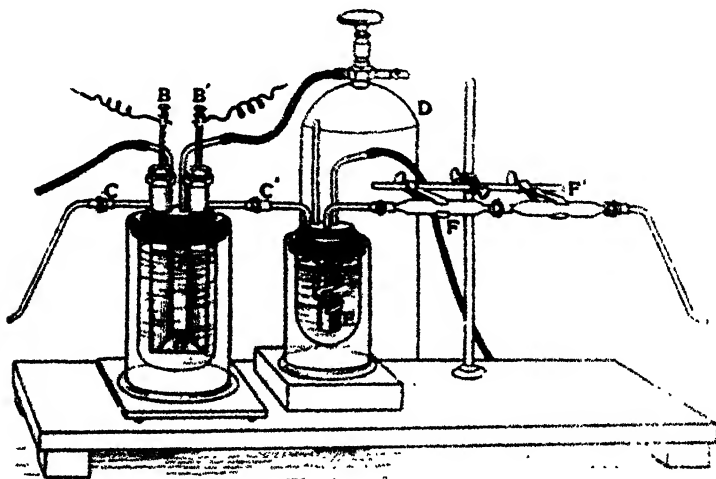


FIG. 51.

under reduced pressure at about  $-50^{\circ}\text{C}.$ ; a large vacuum-vessel (p. 207) would serve conveniently to hold this liquid.

To prepare fluorine, about 200 grs. of anhydrous hydrofluoric acid, and 50 grs. of acid potassium fluoride are placed in the apparatus, one of the fluor-spar plugs being removed for the purpose. For the electrolysis a current of 15 amperes at 50 volts is employed, and about five litres of fluorine is liberated per hour; with stronger currents it is found that the heat generated cannot be removed with sufficient rapidity.

To remove traces of hydrofluoric acid from the fluorine the gas is led through a coil into a platinum vessel E, which is also immersed in a bath of methyl chloride, and subsequently through two drying tubes F, F' containing pieces of fused sodium fluoride.

The hydrogen is led away to a distance through tubes which terminate in an apparatus filled with calcium chloride.

*Preparation of pure hydrofluoric acid, and acid potassium fluoride.*—Pure commercial hydrofluoric acid is taken and partially neutralised (about one-quarter) with potassium carbonate. The product when distilled in a platinum retort, heated to  $120^{\circ}$  C. in an oil-bath, yields an acid free from fluosilicic acid, which is usually present in considerable quantity in the commercial acid. The distillate is divided into two portions, and after neutralising one portion with potassium carbonate, the two are mixed, and the solution of acid potassium fluoride so obtained is evaporated to dryness on a water-bath. To remove the last traces of moisture the platinum basin containing the salt is allowed to remain for a fortnight in a vacuum-desiccator containing sulphuric acid and some sticks of caustic potash; both the acid and potash are changed daily, and the salt is from time to time crushed in an iron mortar.

The dry salt when heated in a platinum retort decomposes, yielding the anhydrous acid (which boils at  $19.5^{\circ}$ , and must be condensed in a freezing mixture) and potassium fluoride. The first portion of the distillate, which contains traces of water, may be rejected.

*Chlorine,  $\text{Cl}_2$ .*—Large quantities of chlorine are most conveniently prepared by treating manganese dioxide with pure hydrochloric acid. The manganese dioxide should have been powdered, boiled with strong nitric acid to eliminate carbonates, and thoroughly washed and dried. The gas may be purified by passage through anhydrous copper sulphate and pentoxide of phosphorus, which must be quite free from lower oxides (see p. 41). All the connections throughout the apparatus should be of glass; no rubber or cork stoppers should be used. If the gas is to be stored, strong sulphuric acid may be used in the gas-holder.

Pure chlorine may be obtained by fractional<sup>b</sup> distillation of the impure gas. Liquid chlorine, which is sold in cylinders, contains little impurity. A small quantity of chlorine can be introduced into a vacuum-tube or other piece of apparatus in the following manner. A bulb containing pure gold chloride,  $\text{AuCl}_3$ , is attached to the apparatus in such a manner that it can be sealed off with a blowpipe flame when the apparatus is exhausted.

After exhaustion the apparatus is shut off from the pump and the bulb is warmed. Pure chlorine enters the apparatus, but on standing it is very slowly reabsorbed by the gold.

This method may be employed in order to obtain a definite quantity of chlorine.

*Nitrogen*,  $N_2$ , is perhaps in actual practice one of the most difficult gases to prepare in a high state of purity. The researches of Lord Rayleigh on the density of that gas, and the subsequent investigation carried out in conjunction with Professor Ramsay, have proved that atmospheric air contains an element, argon, of density approaching 20.

The chief difficulty in connection with the preparation of pure nitrogen lies in the removal of the nitric oxide which is produced in small quantity by most of the reactions in which nitrogen is the chief product. Nitric oxide is an extremely stable compound, and can only be eliminated by passing the gas through a tube containing metallic iron or copper, heated to a redness. The use of iron is to be avoided, since a trace of moisture entering the tube gives rise to the production of hydrogen.

Lord Rayleigh's results show that nitrogen, practically free from nitric oxide, can be prepared by heating a solution of ammonium chloride and potassium nitrite on a water-bath, passing the gas through a tube containing red-hot copper, and subsequently through caustic potash, sulphuric acid, and pentoxide of phosphorus.

If the presence of argon does not materially affect the result, and it is merely required to prepare a quantity of nitrogen in order to carry out some process which it is necessary to conduct in an atmosphere of inert gas, the following method may be applied. Atmospheric air is drawn slowly through a solution of strong ammonia, contained in a wash-bottle, through a tube containing metallic copper heated to a red heat, and finally through a vessel containing strong sulphuric acid to remove moisture and excess of ammonia. The volume of the nitrogen obtained by this process is nearly equivalent to the quantity of air used.

It may be as well to state here, by way of warning, that metals generally are not nearly so inactive with regard to nitrogen as they were formerly supposed to be. Most metals appear to combine slowly with nitrogen, forming nitrides.

*Atmospheric nitrogen* for use in pressure gauges, etc. (pp. 164, 230) may be obtained by passing air through a tube containing copper, and subsequently through caustic potash, etc.

*Carbon dioxide*,  $\text{CO}_2$ .—(a) The liquid which is sold in steel cylinders usually contains as an impurity only dissolved air, which escapes with the first portions of the gas, and water.

(b) The gas may be obtained pure by heating pure dry sodium bicarbonate in a horizontal tube. If the tube is not previously exhausted the heating should be commenced at the *extreme* end, otherwise the air in the tube will not be swept out by the current of gas, but will only escape slowly by diffusion.

(c) A steady current of carbon dioxide may be obtained by heating a mixture of one part of sodium carbonate with three parts of potassium bichromate in a wide hard glass tube. The tube should be only partially filled with the mixture, and should be so inclined that the fused mass does not run down into the open end of the tube. This method has the advantage that no water is produced during the reaction, as in the last case.

(d) Carbon dioxide may be obtained by heating carbonate of magnesium, but in no case should carbonate of manganese be employed. At the temperature at which the decomposition takes place the manganous oxide is capable of reducing the carbon dioxide and water vapour, and producing carbon monoxide and hydrogen. Moderately pure carbon dioxide may be obtained by the action of hydrochloric acid upon marble. Both the acid and the marble may, however, constitute sources of impurity.

*Carbon monoxide*,  $\text{CO}$ .—(a) Concentrated sulphuric acid is heated in a small flask, and small quantities of formic acid, previously boiled to expel air, are run in through a tap funnel.

(b) The gas may also be obtained by heating a mixture containing 50 grams of sodium formate, 300 grams of sulphuric acid, and 150 grams of water.

(c) By heating a mixture of 100 grams of crystallised oxalic acid with 500 grams of concentrated sulphuric acid, carbon monoxide is produced, together with an equal volume of carbon dioxide. The carbon dioxide can easily be removed by passing the gas through a strong solution of caustic potash.

(d) By heating a mixture of 80 grams of pure recrystallised potassium ferrocyanide with 360 grams of concentrated sulphuric acid, a steady stream of carbon monoxide is produced. The



reaction may be stopped by cooling the flask, and started again by the application of heat.

(c) Pure potassium cyanide may be used instead of the ferrocyanide.

The gas should in each case be purified by passage over solid caustic potash, strong sulphuric acid, and pentoxide of phosphorus. Dixon states that it is extremely difficult to remove the last traces of moisture from the gas. Lord Rayleigh determined the densities of samples of gas obtained by methods *b*, *c*, and *d*, and obtained very concordant results (*Proc. Roy. Soc.*, December 9, 1897).

*Nitrous oxide*,  $N_2O$ .—By heating ammonium nitrate to a temperature not above  $258^\circ$ . The salt begins to decompose at about  $170^\circ$  into water and nitrous oxide. At high temperatures nitric oxide is produced. The gas must be passed over potash, and subsequently over sulphuric acid and pentoxide of phosphorus.

Lord Rayleigh obtained pure nitrous oxide for the determination of its density in the following manner. An iron bottle containing liquid nitrous oxide was placed in a freezing mixture, and half the liquid was allowed to evaporate. The remaining nitrous oxide was considered to be free from dissolved nitrogen.

*Nitric oxide*,  $NO$ .—Dilute nitric acid (e.g. 1:1), which has previously been boiled, is run into a flask (Fig. 41) which is connected with tubes containing strong potash solution, solid potash, strong sulphuric acid, and pentoxide of phosphorus. The whole apparatus must be thoroughly exhausted before the introduction of the acid. A strong solution of sulphur dioxide, obtained by passing the gas from a syphon into boiled water, is run into the flask in small quantities, and the mixture is warmed if necessary. It is somewhat difficult to separate traces of the higher oxides, even by fractional distillation.

*Ammonia*.—Pure ammonia may be obtained by heating a mixture of pure ammonium chloride and lime. The gas may be dried by passing it through a long tube containing freshly prepared barium oxide.

The ammonium chloride should not be obtained from any organic source. The salt from gas liquor invariably contains traces of hydrochlorides of organic bases from which it cannot be freed. The so-called volcanic\*ammonia, when genuine, is pure; ammonium chloride can also be obtained free from impurity by passing the ammonia, produced by the action of water on magnesium

nitride, into dilute hydrochloric acid. The latter method does not, however, serve for the preparation of the pure gas, as some of the ammonia is invariably decomposed by the local heating of the nitride in contact with water, and the gas is found to contain both free nitrogen and hydrogen. It can, however, be easily separated from these gases by fractional distillation.

*Phosphoretted hydrogen,  $\text{PH}_3$ .*—The gas cannot be obtained pure by the action of alkali on phosphorus, since traces of hydrogen are produced by the decomposition of the hypophosphite which is a product of the reaction. Hydrogen is also produced by the interaction of phosphides with water.

The gas is most conveniently obtained from the dichloride of cuproso-diphosphonium (Ribau, *C. r.*, **110**, 240, 510), which is obtained by passing phosphoretted hydrogen into a solution of cuprous chloride in hydrochloric acid. The compound can be separated in colourless needles. The saturated solution gives nearly eighty times its volume of phosphoretted hydrogen on heating. The gas may be purified by passage over potash and pentoxide of phosphorus.

Impure phosphoretted hydrogen could easily be purified by fractional distillation.

*Hydrochloric acid,  $\text{HCl}$ .*—By the action of strong sulphuric acid upon fused sodium chloride, or preferably upon ammonium chloride. The salt is placed in a flask (Fig. 41), and the acid is introduced through the tap-funnel, the stopcock of which is lubricated with metaphosphoric acid. The gas must be dried by passage through sulphuric acid, and subsequently through a considerable length of tube containing pentoxide of phosphorus.

*Hydrobromic acid,  $\text{HBr}$ .*—It is easy to prepare pure hydrobromic acid by allowing the aqueous solution of the gas to drop slowly into a flask containing pentoxide of phosphorus. The gas is subsequently allowed to flow through tubes containing the same substance. Care must be taken that the liquid does not come too rapidly in contact with pentoxide, or some of the gas will be decomposed owing to the heat developed during the reaction.

*Hydriodic acid,  $\text{HI}$ .*—Pure hydrogen iodide may be obtained in the following manner (Banuow, *B.*, 1874, 1498). A solution of 10 parts of iodine in 5 parts of an aqueous solution of hydriodic acid is allowed to drop into a flask containing 1 part of red phosphorus. The gas is first passed through a tube containing

red phosphorus. A certain quantity of phosphonium iodide is formed, and must be got rid of by passing the gas through a cooled spiral. The gas is then passed through a tube containing calcium iodide, and finally dried by passage through pentoxide of phosphorus. The gas is easily decomposed by the action of heat or light.

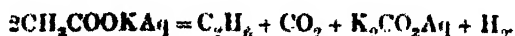
This gas might well be purified by fractional distillation.

*Sulphur dioxide, SO<sub>2</sub>.*—The liquid sulphur dioxide obtained in glass syphons is of a high degree of purity. After rejecting the first portion, a stream of the gas from a vessel containing the liquid may be passed through tubes containing pentoxide of phosphorus directly into the vessel in which it is to be collected.

*Sulphuretted hydrogen, H<sub>2</sub>S.*—The pure gas may be obtained by the action of magnesium chloride upon calcium sulphide in the presence of water (Hebermann, *Ch. J.*, **13**, 314). The water should be allowed to drop slowly on the solids which are powdered and mixed together. Moist sulphuretted hydrogen must not be brought into contact with mercury.

The gas can be condensed in a bulb cooled by solid carbonic acid and ether, and distilled.

*Ethane, C<sub>2</sub>H<sub>6</sub>.*—Murray (*Jour. Chem. Soc.*, 1892, **61**, 10) has carefully investigated the conditions which are most favourable to the production of ethane by the electrolysis of potassium acetate. The decomposition takes place according to the equation—



Ethane and carbon dioxide are liberated at the anode.

A concentrated solution of the salt, about 60 per cent, should be used, with a current of 15 ampères; the surface of the anode should be about 150 sq. cm. Since the yield of ethane decreases considerably with rise of temperature, the apparatus must be kept cool during the experiment. An apparatus similar to that employed for the electrolysis of dilute sulphuric acid might be conveniently used.

The gas when first generated always contains, besides carbon dioxide, traces of oxygen, ethylene, and vapour of methyl acetate. Kuenen (*Phil. Mag.*, 1895, **40**, 177) found that the impurities could be most conveniently removed in the following manner.

The gas was first passed through fuming sulphuric acid into a large gasholder containing soda solution. It then passed through tubes containing fuming sulphuric acid, solid potash, and pentoxide of phosphorus to a compression apparatus, by means of which it was liquified. The liquid was then cooled with solid carbonic acid, and allowed to boil in order to expel the permanent gases. The middle fraction consisted of perfectly pure ethane, the higher boiling impurities remaining on the apparatus.

*Ethylene*,  $C_2H_4$ , cannot be obtained sufficiently pure for the determination of physical constants by the action of sulphuric acid upon alcohol. Sulphur dioxide, carbon dioxide, and monoxide are always among the products of this reaction. The gas can easily be obtained pure by liquefaction and subsequent fractional distillation of the liquid (p. 211).

*Acetylene*,  $C_2H_2$ .—Pure acetylene can only be obtained by liquefying and distilling the gas generated by the action of water on calcium carbide. The gas always contains hydrogen from free calcium, siluretted hydrogen from calcium silicide, phosphoretted hydrogen from calcium phosphide, and aldehyde vapour produced by the condensation of acetylene with water, a reaction which takes place more rapidly in presence of acids. The gas may be freed from phosphoretted hydrogen by passing it through a solution of silver nitrate.

Liquid acetylene can be purchased in cylinders on the Continent.

*Methane*.—From sodium acetate (1 part) and barium oxide (4 parts). The mixture must not be heated too strongly. The gas is purified by passage through caustic soda and strong sulphuric acid.

By the action of zinc-methyl on water. The gas is purified by passage through water, caustic soda, and strong sulphuric acid. In order to avoid risk of contamination by introduction of higher hydrocarbons, the zinc-methyl must be prepared by the action of the zinc-copper couple on pure methyl iodide.

*Silicon tetrafluoride*,  $SiF_4$ , can easily be obtained by heating a mixture of silica and sodium fluoride with strong sulphuric acid; the silica should be present in excess. The apparatus should be quite dry, and the gas should not be allowed to enter the pump.

*Methyl chloride*,  $CH_3Cl$ , can be purchased on the Continent,

but is somewhat difficult to obtain in England. It boils at  $-24^{\circ}$  C., and is much used as a refrigerant.

*Ozone,  $O_3$ .*—Although it is impossible to obtain ozone free from oxygen, it is convenient to include in this chapter a description of the methods employed in manipulating it. A mixture of ozone and oxygen may be obtained by subjecting pure oxygen to the influence of the silent discharge. Nitrogen must be absent, since the conditions which favour the production of ozone lead also to the formation of oxides of nitrogen. The gas must not be brought into contact either with rubber or with mercury, both of which are attacked by ozone. The gas does not, however, act upon paraffin, and stopcocks may be lubricated with metaphosphoric acid.

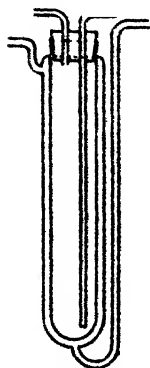


FIG. 52.

The quantity of ozone, that is to say the percentage of ozone in the mixture, varies with the nature of the discharge, with the temperature, and with the quantity of moisture present in the gas. The following are the more important points to be kept in mind in designing the apparatus:—

- (i) The ozoniser must be kept cool.
- (ii) The ozoniser must be made of thin glass of uniform thickness.
- (iii) The two surfaces between which the discharge is passed, should be as close together as possible (Shenstone and Priest, *Chem. Soc. Jour.*, 1893, **63**, 952).

A modified form of the apparatus originally designed by Brodie may be made to fulfil these conditions (Fig. 52). The body of the apparatus, which is similar in construction to the vacuum-vessels used to contain liquid air, consists of two concentric cylinders closed at their lower ends and sealed together. Two tubes are sealed into the outer cylinder, and serve as leads for the gas. The apparatus is partially immersed in a deep vessel of water; the discharge is passed through the gas contained in the space between the two cylinders by immersing the ends of the secondary leads from a coil in the water in the jacketing vessel, and in that in the inner cylinder.

For the production of ozone in large quantity the Andreoli ozoniser appears to be the most efficient. It consists of a number

of flat rings of pewter toothed on the inside, and connected longitudinally by strips of metal to form a cage. The cage fits over an exhausted glass cylinder, with a long electrode sealed into it, so closely that the points touch the glass everywhere. The leads from the coil are connected with the cage and with the electrode of the vacuum-tube, and the whole apparatus is placed inside the vessel in which the ozone is to be produced. The exhausted tube may be replaced by one through which a current of water circulates, so that the ozone is actually produced in contact with a cooled surface.

With regard to the nature of the discharge, Shenstone and Priest state that the difference of potential should not be too great, and that the interruptions should not exceed one thousand per minute. It appears, however, that the intensity of the discharge should bear some relation to the rate of flow of the gas, and that for a rapid current a high potential may be used with advantage; in the latter case a large coil should be employed (see also p. 241).

## CHAPTER VI

### READING INSTRUMENTS

General remarks—The mirror scale—The reading telescope and cathetometer—  
Illumination of scales—Graduation of tubes and scales—Capillarity—Capillary  
depression of mercury—Sticktion—Adjustment of the level of mercury.

NEARLY all the measurements with which we are concerned in dealing with gases, consist in the determination of the position of the surface of the liquid in the vessel in which the gas is confined.

The readings are taken either with regard to a fixed point, to graduations on the outer surface of the glass, or to a scale placed close to it. Since the surface of the liquid is invariably curved, the reading usually involves the determination of the position of the middle point of the curved surface, with regard to a scale which is distant from it by at least the radius of the tube, and unless the eye of the observer is exactly on a level with the surface of the liquid, the accuracy of the observation will be seriously affected.

*The mirror scale (Jolly).*—In reading barometers, manometers, etc., it is usual to employ a glass scale ruled in millimetres. The scale is etched on the surface of a strip of glass about 5 mm. in thickness, which is then silvered on the second surface. When the eye is placed somewhat above the level of the surface of the liquid, the image of the meniscus is seen reflected in the mirror slightly above the true surface, and the divisions of the scale do not appear to coincide with their reflected images. In taking a reading, the eye must be brought down exactly to the level of the surface of the liquid, when, if the scale is perpendicular, the meniscus and divisions of the scale will exactly coincide with their reflected images. To facilitate

reading, a piece of white paper should be held on one side of the scale, and a lens of low magnifying power should be used. A lantern covered with parchment paper may be used for taking readings at night.

It has been suggested that inaccuracy in the observations may result from irregularities in the glass surfaces about the edges of the lines ruled on the glass surface. The error would be very small in any case, and would entirely disappear if the scales were so placed that the ruled lines only extended half-way across the field. The total error might, however, in this case be still greater, as small irregularities are more likely to occur at the end than in the middle of the lines. In any case the lines should be made as fine as possible.

Scales etched upon glass, and illuminated from behind, are more convenient for use with a telescope or cathetometer (p. 58).

*The reading telescope* is usually employed in making accurate observations of pressure, volume, etc. The telescope consists of a combination of an object lens and a negative eyepiece containing a spider line or cross-wire. A pair of convex lenses is often introduced into the system to act as a rectigraph. A level is attached to the top of the telescope.

The telescope, which is mounted on a stand resting on three levelling screws, should be capable both of vertical and of horizontal motion. In its simplest form it is carried on a mount, which slides on the vertical rod which forms the stand, and which can be clamped in any position. The mount may be so constructed that the telescope may be rotated about the vertical axis, and a screw arrangement for adjusting the telescope in the vertical position may be added. The latter, however, unless very well constructed, will prove worse than useless.

A telescope of this description may be used in reading the position of the surface of the liquid in a glass vessel, with regard to the graduations on its outer surface, or to a scale placed either behind it, or so close to it, that both the surface of the liquid and the scale are in the field at once. The telescope is placed at such a distance from the apparatus, that both points of observation are in focus at the same time, the cross-wire is adjusted to the surface of the liquid, and its position with regard to the scale is determined. It is not advisable to employ a cathetometer,



an instrument in which the scale is attached to the telescope, in making observations of this kind. Unless the instrument is very well constructed, and is made very heavy and rigid, considerable errors may be introduced.

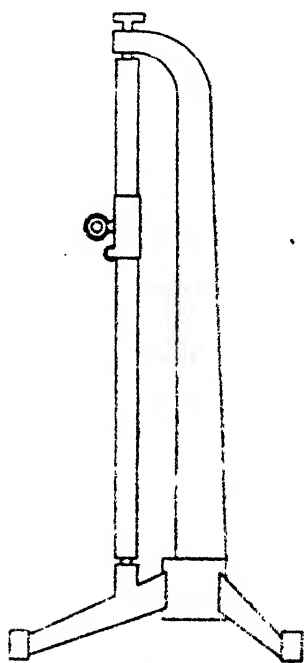


FIG. 53

Sometimes the scale cannot be placed so close to the instrument, that the cross-wire of the telescope can cover both the surface of the liquid and the graduations at the same time. In this case the telescope must be so arranged that it can be turned horizontally so as to cover each of the objects in turn without vertical deviation. In order to secure this object, the telescope stand may be so constructed, that the whole of the pillar on which the telescope moves may be made to turn about its vertical axis (Fig. 53). The setting of the instrument may be tested by observing the height of the liquid (mercury, or water) in three vertical glass tubes connected to a common reservoir,

and placed on the circumference of a circle, in the centre of which the telescope is placed. Lord Rayleigh has described a reading telescope in which the vertical support is pivoted between fixed plates on the floor and ceiling of the laboratory.

If an accurately constructed telescope is not available, errors may be eliminated by reading from two scales placed one on either side of the apparatus.

*Illumination of scales, etc.*—In a series of measurements involving the determination of the height of a column of mercury by means of a scale and telescope, it is necessary to take the precaution that light always comes from the same position with regard to the surface of the mercury. The top of the meniscus may appear a few tenths of a millimetre higher or lower according as the light comes from a window at the side, or from a lamp placed behind the instrument. This difficulty may be overcome by using only diffused light. A piece of ground glass or parchment paper placed behind the instrument and illuminated either

by daylight, or by a flame placed at some distance from it, has been found to give very good results. In an investigation in which it was necessary to use a glass scale about one metre in length, the back of the scale was covered with a strip of ground glass, and an electric lamp, which could be adjusted to the height of the mercury column, was used as the source of light. A strip of silvered glass placed at an angle behind the instrument has been sometimes used with satisfactory results.

*Graduation of scales, etc.*—The dividing engine is, of course, the most efficient and accurate instrument by which a scale may be ruled on metal or glass. The gear, which is carried on a traveller, is moved by means of a screw of very regular pitch attached to a divided head. The length of the lines is usually regulated mechanically, so that every fifth line may be made longer than the others. The instrument must be kept at constant temperature during the ruling of a scale.

Since the dividing engine is a very expensive and delicate instrument, it is not found in every laboratory; it will be well, therefore, to describe one or two simple methods for dividing scales on glass.

Scales may be ruled on glass by means of a diamond, or etched with hydrofluoric acid. The first method gives the finer lines, but unless the glass is thick it is liable to crack along one of the divisions. The second method is most usually employed; the glass is first warmed, and then coated with a thin even layer of yellow *bees-wax* or some substance of a similar consistency. The scale is then ruled and figured, and a piece of cotton wool soaked in concentrated hydrofluoric acid is passed several times lightly over the surface. The excess of acid is removed by washing with water; the scale is then warmed, and the wax is removed. The graduations may be made more distinct by rubbing a little red lead mixed with shellac varnish into them, and removing the excess with a rag.

Short scales may be conveniently ruled in the following manner. A steel rule about 4 cm. wide is divided into millimetres along both edges of the same surface so that the divisions correspond. The rule is fixed on a board so that its surface lies a little above the surface to be ruled. The plate, or instrument which is to be divided, can be fixed in position by means of a little pitch. The traveller is shown in Fig. 54. It consists

of a triangular plate of brass, along one edge of which is fixed a narrow projecting strip which serves as a guide. At right

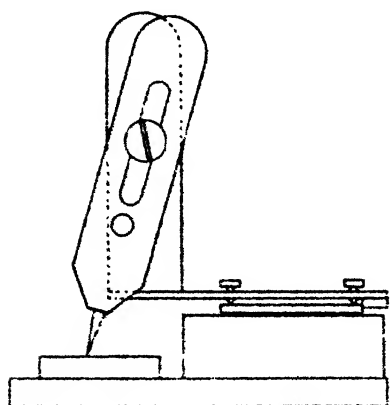


FIG. 51.

angles to this strip, two pointed screws pass down through the plate, so that when the strip is pressed against the edge of the rule, the screw points fall into corresponding divisions of the scales. The plate carries an upright which serves to direct the ruling needle, which is carried on a strip of brass held against the face of the upright by means of an adjustable screw working in a vertical slot. The upright is so placed that when the needle

is vertical it lies at about 2 cm. from the edge of the rule. A small knob projecting from the strip which carries the needle serves as a handle.

In using the instrument, the plate or tube to be divided is placed in position, the position of the traveller is regulated by the left hand, and the needle is drawn across the surface which is being ruled so as to cut through the wax. In order to regulate the length of the lines the surface may be marked longitudinally with Indian ink before the wax is applied.

It is not easy to rule scales of any length by means of this instrument on account of the expansion of the steel scale. If a long scale is used it should be fixed to the board at one end only, and the work should be conducted so as to employ a section of it as near to this end as possible.

Ostwald describes a convenient method of dividing short scales in his *Physico-Chemical Measurements*.

**Capillarity.**—In measuring the pressure on a gas confined in a tube of small internal diameter, or in determining the true difference of level between the liquid in two tubes of different diameters, it is necessary to make a correction for capillarity.

In the case of a liquid which wets the glass this becomes merely a matter of calculation for tubes of small diameter. Where  $\rho$  is the density of the liquid,  $\gamma$  its surface tension,  $h$  the height to which it rises in the tube, and  $r$  the radius of the tube:—



Stöckli (*Wied. Ann.*, 1898, 516) has observed that when a gas is allowed to enter a vessel containing mercury the surface tension is temporarily increased, but regains its normal value after some minutes. The phenomenon is attributed to a static electrical effect connected with the condensation of the gas on the surface of the mercury. The correction for capillarity appears in any case to be of such an uncertain nature that it should, when possible, be eliminated.

*Sticktion*.—In experiments involving the use of tubes of small diameter containing mercury a difficulty is experienced to which the term *sticktion* has been applied. Its exact nature has not been explained, but appears to be due to a *tendency* of the mercury to wet or adhere to the glass.

If a vertical capillary tube is connected by a piece of rubber tube to a reservoir containing mercury, which is slowly raised, the mercury will rise in the capillary tube in a series of jerks. Further, if the reservoir is brought to rest, and the capillary tube is tapped with the finger, the mercury will not always come to rest in exactly the same position. The phenomenon becomes more marked if the glass is not quite clean.

In tubes of larger diameter the mercury appears to adhere to the walls at the edges of the meniscus. If the glass is perfectly clean this only occurs so far as to alter the form of the meniscus when the mercury is rising or falling, an effect which may be attributed to friction alone. In order to obtain concordant results, observations in the same series of experiments should be taken either after raising, or after lowering the mercury to the fiducial point as may be found most convenient. If the reading is to be taken with regard to a scale after the mercury has been brought to rest, the tube may be tapped. Continuous tapping by means of the hammer of an electric bell has been found to answer successfully.

In some recent experiments on the rate of diffusion of gases, it was necessary to measure the rate of fall of a column of mercury from one fixed point to another. It was found that by introducing a drop of strong sulphuric acid or glycerol into the tube the effect of sticktion was entirely eliminated.

In order to bring the level of the mercury in a burette to a fixed point, the height of the reservoir may be adjusted by means of a cord passing over a pulley or by placing it on an adjustable

clamp. The final adjustment may be made (Fig. 56) by means of a closed glass tube which, passing fairly loosely through a cork in the mouth of the reservoir, may be forced down into the mercury. The burette is sometimes connected with the reservoir through a tap. The reservoir is first raised till the mercury lies a little below the mark,

the tap is then closed, and the final adjustment is made by compressing the rubber tube with a broad wooden clamp attached to the table.

A screw plunger (Fig. 57) has been used by Baly and Ramsay in connection with the M'Leod gauge. A cylindrical iron block *c* was cemented into the upper and wider portion of the glass apparatus *d*. The plunger *a* was screwed through the block, and the small screw *b* passed through the larger plunger, and served as a fine adjustment. It was found that if the screws were well greased considerable pressure in the vessel *d* was required to force the mercury between the threads of the screws. The preliminary adjustment of the mercury in the gauge was made by means of an ordinary reservoir and rubber tube, which was connected to the apparatus through a tap. The tap was subsequently closed, and the final adjustment was made by means of the screws alone.

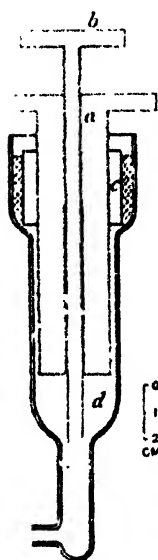


FIG. 57.

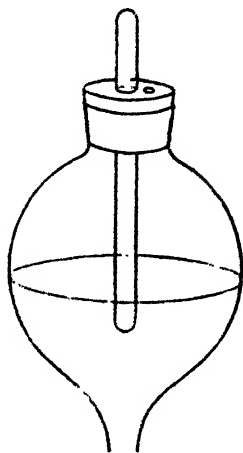


FIG. 56.

## CHAPTER VII

### MEASUREMENT OF VOLUME

Measurement of the volume of gases - Gas analysis.

IN measuring the volume of a gas, it is of course necessary to take into consideration its temperature and the pressure under which it is confined. For the purposes of gas analysis it is possible, however, to neglect the variations from the laws of Boyle and Gay-Lussac, since they lie outside the limit of accuracy of most of the processes involved, and to assume that the equation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

holds good in its simplest form.

The law of mixtures can also be assumed within the same limits.

A special case, which occurs in most of the processes in gas analysis, consists in the application of the correction for the pressure of water-vapour in a gas. Most of these processes consist in treating a gaseous mixture with aqueous solutions of different reagents in order to absorb particular constituents. The gas becomes saturated with water-vapour at the surface of the solution, and as this is a function both of its nature and its concentration, it is practically impossible to calculate the quantity of water in the gas, and so determine the volume of dry gas which is present. If the gas is to be measured dry, it may be drawn through a tube containing pentoxide of phosphorus attached to the pump, and measured in a dry burette. In order to eliminate the source of error due to partial saturation, the gas should be brought into contact with pure water at the tempera-

ture at which it is measured, by introducing a few drops of pure water into the measuring burette.

It is unlikely, except in a perfectly clean and dust-free vessel, that a gas would long remain supersaturated.

The vapour pressure of water may be determined from the following table:—

#### VAPOUR PRESSURES OF WATER (see also p. 238)

Temperature.	Pressure.	Temperature.	Pressure.
8°	8.017 mm.	17°	14.421 mm.
9°	8.574 ..	18°	15.357 ..
10°	9.165 ..	19°	16.346 ..
11°	9.792 ..	20°	17.391 ..
12°	10.457 ..	21°	18.495 ..
13°	11.162 ..	22°	19.659 ..
14°	11.908 ..	23°	20.888 ..
15°	12.699 ..	24°	22.184 ..
16°	13.536 ..	25°	23.550 ..

If it is necessary to measure the gas in contact with a solution, the correction to be applied will, of course, be less than for pure water at a corresponding temperature. The vapour pressures of aqueous solutions of the commoner acids, alkalis, and salts have been determined by Bunsen and others. Tables will be found in Karl von Bucher's *Physikalisch-chemische Tabellen*.

When a gas is measured at a fairly high temperature in a vessel containing mercury, the vapour pressure of mercury must also be considered. The following figures have been taken from the determinations of Ramsay and Young:—

#### VAPOUR PRESSURES OF MERCURY

Temperature.	Pressure.	Temperature.	Pressure.
40°	0.008 mm.	200°	17.02 mm
50°	.015 ..	220°	31.96 ..
60°	.029 ..	270°	123.9 ..
70°	.052 ..	280°	157.4 ..
80°	.093 ..	290°	198.0 ..
90°	.160 ..	300°	246.8 ..
100°	.270 ..	310°	304.8 ..
120°	.719 ..	320°	373.7 ..
140°	1.763 ..	330°	454.4 ..
160°	4.013 ..	340°	548.6 ..
180°	8.535 ..	350°	658.0 ..

Mercury boils at 357° (Crafts, P. A. [2], Beibl. 7, 183).



In order to account for the chemical changes which gases undergo it is necessary to assume Avogadro's hypothesis. The assumption is justified within the limits of ordinary analysis. In the case of the volumes of oxygen and hydrogen in electrolytic gas, the error is only about one part in a thousand (see p. 135) if proper precautions are taken.

After measuring the gas and applying the corrections for temperature and pressure, its weight may be found by multiplying by the weight of unit volume (p. 117). In this case it is necessary to determine the *absolute* volume of the gas (see p. 119). In order to determine the percentage composition of a gas it is only necessary to know the *relative* volumes of its constituents.

The volume which a quantity of gas occupies under standard conditions may be determined by one of two methods, which for ordinary purposes may be considered as identical:—

(i) By measuring its volume in a graduated instrument under known conditions of temperature and pressure.

(ii) By measuring the pressure which it exerts when expanded or compressed to fill a known volume under known conditions of temperature.

The constant pressure method (i) will be considered first, for although it is the less accurate, the apparatus employed and methods of manipulation are simpler.

A very simple and convenient form of gas burette is shown in Fig. 58. The apparatus consists of a syphon gas-pipette with a two-way stopcock, graduated in cubic centimetres from a mark on the millimetre bore tube near the tap. Two platinum wires are sealed through the glass as near to the top as possible. This, of course, makes it quite impossible to measure very small quantities of gas accurately, but when rough analyses only are required it is convenient to be able to carry

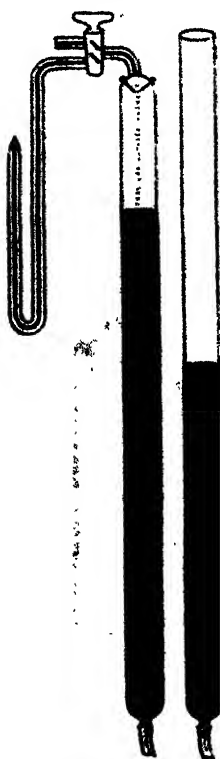


FIG. 58.

out the whole operation with one piece of apparatus. The reservoir is cylindrical, and of the same diameter as the burette.

A much more accurate form of the apparatus is shown in the next figure. The burette is of the same form, but a tube of about 7 mm. diameter, connected with it at its lower end, and terminating in a stopcock, renders it possible to determine the pressure on the gas with greater accuracy. Both the burette and side-tube are enclosed in an outer jacket through which water is constantly circulated, and although the difference in the size of the two tubes renders it necessary to apply a correction for capillarity, the readings are more easily taken, and the error due to the difference of temperature between the mercury inside and outside the water-jacket is practically eliminated. The temperature is determined by means of a thermometer placed inside the water-jacket.

The operation of measuring a gas is conducted in the following manner. The reservoir is first raised till the mercury rises above the stopcock on the side-tube, which is then closed. The tube containing the gas is then brought over the syphon of the burette, the reservoir is lowered, and part, or the whole, of the gas is taken over. Mercury is then drawn into the syphon up to the mark. The reservoir is then raised till the mercury in the side-tube, which is now opened to the air, is exactly on the level with the surface of the mercury

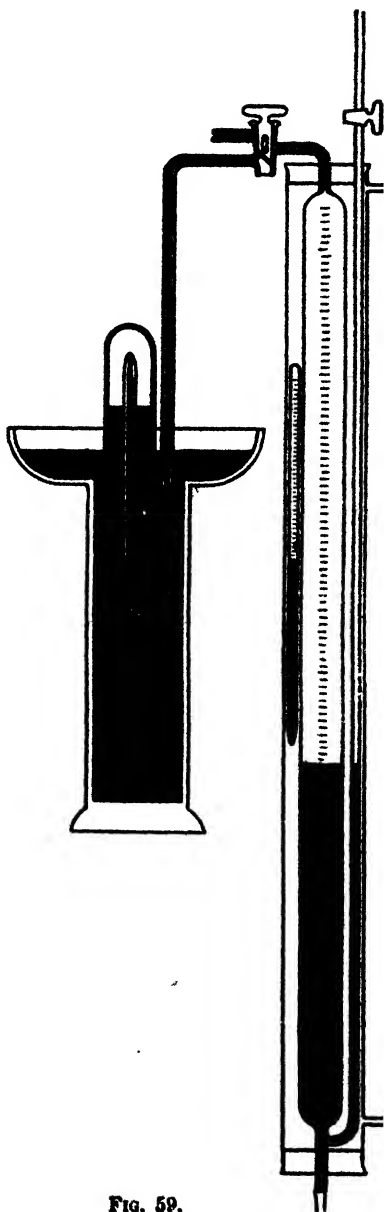


FIG. 59.

in the burette. The final adjustment may be made by one of the methods described on p. 62. The volume of the gas is read off by means of a telescope, and the temperature of the water in the jacket is observed. The true volume is determined from the equation

$$V = \frac{v \times B + p \times 273}{273 + t} \times \frac{273}{760},$$

where  $v$  = observed volume.

$B$  = corrected barometric height.

$p$  = correction for capillarity.

$t$  = observed temperature.

The value of  $p$ , the capillarity, may be determined by allowing both the syphon and side-tube to stand open to the air, and reading off the difference of level between the mercury in the two tubes by means of a telescope and a scale placed behind the burette. It is usual to graduate a burette of this kind, when accurate work is required, in millimetre divisions. The value of a division in different parts of the scale is determined by a method described on p. 75, and the direct readings are converted into cubic centimetres before the corrected volume is calculated.

The same instrument may be used for the determination of the volume of a gas by the second method. In this case the side-tube is also divided in millimetres, and the relation between the graduations on the two scales is known, so that the difference in level between the surfaces of the mercury in the two tubes can be determined from the observations.

To take a reading by this method the reservoir is adjusted till the surface of the mercury in the burette coincides exactly with one of the graduations. The height of the mercury in the side-tube is then observed, and from it the difference of level of the mercury in the two tubes is directly determined in the following manner. Suppose that in some particular instrument, in which the burette and side-tube are both graduated in millimetres from the top, it is found that the 20 mm. mark on the burette corresponds to 23.7 mm. on the side-tube. If in any particular reading the observed difference of level is  $n$  mm., the pressure under which the gas is confined will be  $B + p \pm (n - 3.7)$  mm. This method of reading is more accurate than the last, but if a large series of measurements are to be made the calculation of the results becomes somewhat more complicated.

When the apparatus is employed in gas analysis, the gas, after its volume has been measured, is transferred either directly or in a gas-tube to the apparatus containing the reagent with which it is to be treated. It is very important that the reagent should not enter the measuring burette, which should contain a trace of water only; if the reactions are carried out in gas-tubes (pp. 26, 27) a separate gas-pipette (p. 28) should be used in separating the liquid and gas, which should be brought to the burette in a clean tube.

*Constant-volume burette for accurate gas analysis.*—Several forms of this instrument have been described by Hempel, Frankland, and others. They all consist ultimately of a burette which is connected directly with a mercury reservoir and with a barometer. The gas is introduced into the burette, and the mercury reservoir is adjusted until the mercury in the burette is brought to the level of some fiducial mark; the difference of level between the mercury in the burette and the top of the column of mercury in the barometer indicates the pressure exerted by the gas when occupying a known or definite volume. From this it is possible to calculate the volume of the gas at normal pressure. Unless the absolute volume of the gas is required, the volume of the burette need not be known; the relative volumes of the constituents of a mixture will of course be proportional to the observed pressures.

In order to simplify the calculation of the results of the analysis of a gaseous mixture it is convenient to maintain the burette and barometer at constant temperature during a set of experiments. To eliminate the correction due to the pressure of water-vapour in the gas, both the burette and the space above the mercury in the barometer should contain a few drops of water.

A convenient form of constant-pressure burette, and one capable of giving results of the highest accuracy, has been devised by Mr. G. N. Huntley.

The burette *a* (Fig. 60) in which the gas is measured contains three opaque glass points (see p. 77), and the volumes of the spaces above the mercury when its surface is in contact with each of the three points is accurately known. The burette is connected with a barometer *b* and with a mercury reservoir: both the burette and barometer are enclosed in water-jackets. The barometer may be sealed directly to the T-tube below the burette, but as the apparatus so constructed is very rigid it is usually found more



FIG. 60.

convenient to insert a piece of rubber tube. In order to eliminate danger from leakage the junction may be enclosed in mercury (p. 20).

The burette and barometer are fixed on a wooden stand so that a mercury-trough (p. 26) may be brought below the syphon; a glass scale is fixed behind the barometer, and is so arranged that the readings can be taken by means of a telescope, standing on the table by the side of the apparatus.

The burette should be calibrated before it is placed in position. A capillary tap is sealed to the bottom of the burette in place of the T-tube; the burette must of course be placed in the water-jacket before the tap is sealed to it. The burette is placed in a vertical position and a current of water allowed to flow through the jacket, it is then filled with mercury by means of a funnel and rubber tube attached to the lower tap.

When the temperature has become constant, the upper surface of the mercury is brought to the mark on the capillary tube just inside the two-way tap. The lower tap is then closed, and the rubber tube is removed and the funnel is emptied. The rubber tube is then reattached, the tap is opened, and mercury is allowed to flow into the funnel till the surface falls below the upper glass point. The funnel is then again raised and mercury allowed to flow back into the burette till the glass point just touches the surface, as seen by the coincidence of the point with its reflected image. The tap is then again closed and the mercury in the rubber tube and funnel run into a glass vessel and weighed. This operation is repeated in order to determine the volume contained between the lower points and the mark near the stopcock.

It is necessary to adopt this method

of calibration since, if glass points are used, the surface of the mercury must be raised till it touches the point in order to take a reading. If the mercury is lowered it appears to attach itself to the point, and does not break away till the true level of the mercury is 0.1 mm. or more below the point.

After fixing the burette and barometer tube in position the barometer tube is filled with mercury by raising the reservoir, or compressing the air inside it, till the mercury fills the chamber and the cup above it. Before closing the top of the barometer by means of the ground-glass stopper and reducing the pressure, a few drops of water are introduced; the top of the barometer is effectually sealed by means of a small quantity of mercury poured into the cup.

It is next necessary to determine the position of the glass points with regard to the scale, which should be fixed so that its position shall remain constant with regard to the burette. This may easily be done by means of a telescope with a cross-wire if the burette lies close to the scale. If the burette and scale lie far apart, the level of the mercury in the barometer should be determined when the top of the barometer is open and the mercury in the burette lies in contact with one of the points. Or the burette may be filled with mercury, and the reservoir lowered so that a vacuum is produced in both parts of the apparatus. In both the latter methods the correction for capillarity is eliminated; in the first it must be applied separately.

As a separate check on the values obtained for the volumes of the spaces from the mark on the capillary tube to the three points, the following experiment may be performed. A small quantity of air is drawn into the burette, mercury is drawn into the capillary till it reaches the mark, and the mercury is adjusted in succession, to each of the three points. The three readings of pressure should be proportional

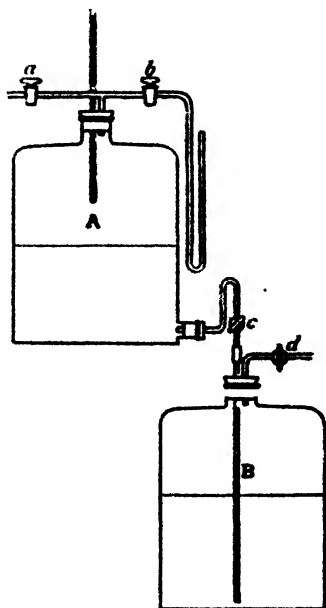


FIG. 61.

to the volumes obtained by weighing with mercury, supposing that the temperature throughout the apparatus is constant and uniform, and that consequently the correction for the pressure of water-vapour and capillarity can be neglected.

Julius Thomsen (*Zeit. An. Chem.*, 1896, 1) has described a very accurate method for measuring large volumes of gas. The gas is introduced through the stopcock *a* into the reservoir *A* which also communicates with a water U-manometer through the stopcock *b*. The volume of water in *A* can be adjusted by opening the stopcock *c* and altering the pressure in *B*, which communicates with a large gasholder through *d*. The water is saturated with the gas to be measured. *B* and the large gasholder are filled with the same gas. The volume of gas in *A* is determined by disconnecting it from *B* and weighing it before and after the experiment.

## CHAPTER VIII

### CALIBRATION, ETC.

Calibration of measuring vessels, etc.

SINCE the glass tubes from which gas burettes and other pieces of apparatus are made are rarely, if ever, truly cylindrical, it is often necessary to determine not only the total capacity of the apparatus but the volume corresponding to each division of the scale. The volume of the apparatus may be calculated from the weight of mercury which fills it at temperature  $t$ . Where  $W$  is the weight of the mercury in grams and  $V$  its volume in cubic centimetres,

$$V = \frac{W(1 + 0.0001815 t)}{13.596}$$

If water is used instead of mercury the volume may be determined from the following table in which the volumes of one gram are expressed in cubic centimetres:—

0°	1.000126	16	1.001025
1°	070	17°	1193
2	030	18°	1373
3°	007	19°	1564
4°	000	20°	1768
5°	008	21°	1981
6°	031	22°	2204
7°	069	23°	2438
8°	122	24°	2681
9°	188	25°	2935
10°	260	26°	3199
11°	363	27°	3472
12°	470	28	3788
13°	590	29°	4045
14°	722	30°	4346
15°	867	31°	4656



The weight of a litre of water at  $4^{\circ}$  C. is taken to be 1000 grams. This is not, of course, exactly true for the standard, the Paris kilogram, but it serves as a convenient standard for physical observations, and the results are always capable of further correction. The actual results for the weight of a litre of water vary between 1000.013 and 999.88 grams, a difference of 0.0015 per cent.

Assuming the density at  $4^{\circ}$  C. to be unity, Scheel (*Wied. Ann.*, 1892, **47**, 400) has found that the density at  $0^{\circ}$  C. is 0.9998748.

*Calibration of the simple gas-measuring tube.*—The tube is carefully cleaned and fixed in a vertical position, mouth upwards, in a clamp. A reading telescope is placed at such a distance that the graduations on the surface of the tube, and the top of the meniscus of the liquid in the tube, can be distinctly seen at the same time.

Successive quantities of mercury, which have been either weighed or measured, are introduced into the tube, and the position of the meniscus is read off after each addition. The mercury should be poured into the tube through a funnel, which is drawn out in the blowpipe flame to a sufficient length to reach to the bottom of the tube. If any air-bubbles are formed between the mercury and the glass they may be removed by means of a long strip of wood.

The quantities of mercury which are introduced may be conveniently measured in the following manner. The edges of a small thick-walled glass tube are ground to fit a glass plate; wooden handles are cemented both to the tube and to the plate. The tube is filled with mercury and the plate pressed on to the top of it while the tube is held over a basin. The plate is then removed, and the mercury is poured into the tube, which is being calibrated.

In this way the capacity of the tube between any two divisions may be determined, but it is not possible to find directly its capacity to any division when it contains a gas confined over mercury. We know the volume  $abdb'$ , we require to know the volume  $acdc'$ , and the difference between these two volumes is  $bdb'cdc$ .

While the tube is still fixed in the clamp the position of the meniscus is read, and a drop of mercuric chloride is allowed to

fall on the surface of the mercury. The surface now becomes flat, and the difference  $\Delta$  between the two readings is equal to half the volume  $bdb'c'dc$ . In order then to obtain the volumes of the tube with regard to the graduation when the closed end is uppermost, it is necessary to add  $2\Delta$  to the values first obtained.

When it is possible it is advisable to avoid the necessity of applying the correction for meniscus, which is difficult to determine accurately, and to calibrate the instruments in the position in which they are used. In the case of the simple gas burette (p. 66), a capillary tap is sealed to the lower tube, and the burette is filled to the mark near the tap with mercury by means of a funnel and rubber tube. Successive quantities of mercury are then run out into a small flask and weighed, and the position of the meniscus is determined at each weighing; the side of the burette should be tapped with the finger before the reading is taken in order to make sure that the meniscus takes its normal form. If the burette is fitted with a side-tube for levelling the operation is similar. The side-tube is completely filled with mercury, and the tap at the top of it is closed; if no air-bubbles are present none of the mercury in the side-tube runs into the burette, although the difference of level in the two is considerable.

While a burette or similar piece of apparatus is being calibrated it must be kept at constant temperature, preferably by means of an outer tube through which a current of water is flowing.

From the telescope readings and weights of mercury the capacity of the instrument in cubic centimetres can be directly calculated. The results may then be plotted on a curve from which the volume corresponding to any numbers of divisions may afterwards be determined. If the burette or tube is truly cylindrical the curve will be linear. This is never actually found to be the case, but the error may be so small as to render it negligible for most purposes.

The volume may be conveniently expressed in grams of

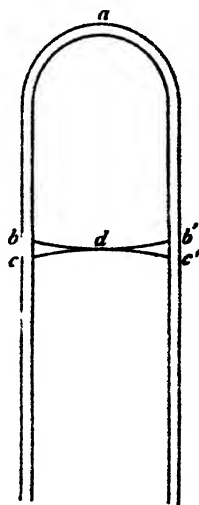


FIG. 62.

mercury when comparative measurements only are required. If several pieces of apparatus are employed, it is important that the volumes are all ultimately referred to the same standard weights (p. 119).

*Calibration of a capillary tube.*—Capillary tube of regular bore is very difficult to obtain, as the motion given to the glass while it is being drawn results as a rule in the formation of alternate wide and narrow sections. Lead-glass tube is usually more regular than soda-glass tube.

(i) *When the tube is open at both ends.*—The tube should either be graduated on the glass, or the position of different points in the tube should be determined by relation to a mark on the tube and to a mirror scale on which the tube is laid. If the readings are to be taken with relation to graduations on the tube a vertical reading telescope should be used, or if this

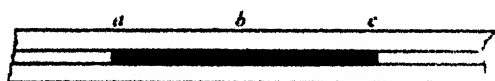


FIG. 63.

instrument cannot be obtained a sheet of silvered glass must be placed underneath it.

In order to determine the volume of the tube a thread of mercury about 2 cm. long is drawn up into it and its length  $a$  is measured at different points in the tube; the values so obtained are plotted against the position of the middle point,  $b$ , of the thread.

Since the ends of the thread of mercury are curved surfaces it is necessary to apply a correction for meniscus before the true volume occupied by the mercury can be determined. If the capillary is less than 0.5 mm. in diameter the meniscus may be taken to be hemispherical, and if the surface were flattened, the cylinder of mercury which would be formed would only have the height  $\frac{2}{3} r$ , where  $r$  is the radius of the tube. It is necessary, therefore, to subtract  $\frac{2}{3} r$  from the length of the thread in order to determine its true length. If the tube is more than 0.5 mm. in diameter the height of the meniscus,  $h$ , must be separately determined. The correction then becomes  $\frac{2}{3} h$ . The radius of the tube may be measured by means of a microscope with a micrometer eyepiece, or in the case of very fine capillary tube may be calculated sufficiently closely on the assumption that the volume of a section of the tube may be directly calculated from the observed length and weight of the mercury thread.

The mercury is finally run out into a small glass vessel and weighed.

A simpler and probably more accurate method of calibrating capillary tubes is as follows. A short thread of mercury is drawn into the tube and its position is adjusted so that one end of it is close to the first division; its length is determined and it is run into a crucible and weighed. A second and somewhat longer thread is then drawn into the tube, and its position is adjusted till one end lies nearly in the same position as in the first case; the length and weight are again determined. This operation is repeated with longer and longer threads until the capacity of the whole tube has been determined.

(ii) *When the tube is closed at one end.*—Where it is possible the calibration of the greater portion of the tube should be carried out before the tube is closed. In order to determine the volume of the closed end of the tube a little mercury is introduced as before and

the enclosed air is sucked out by means of a piece of glass

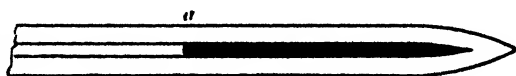


FIG. 64.

tube drawn out to hair thickness. The length of the thread is then determined, and the value of  $\frac{4}{3} r$  is subtracted to allow for the meniscus at *a*. The fine glass tube is again introduced into the capillary, and the mercury is blown out into a glass vessel and weighed.

(iii) *If the capillary is closed at both ends*, as in a thermometer, it is only possible to determine the relation between the diameter of the tube in different parts. This condition is not likely to occur in the manipulation of gases, but a description of the process commonly employed for the calibration of such instruments can be found in Ostwald's *Physico-Chemical Measurements*.

*Calibration of instruments in which an opaque glass point is used as an indicator.*—As has already been stated, the most accurate method of bringing the surface of the mercury in a vessel to a certain level is by the use of the black glass point used by Von Jolly in the analysis of air. Since the mercury must always be raised (p. 71) till it just touches the glass point, special methods of calibration must be employed.

Sometimes (p. 119) it is necessary to fill the apparatus with

mercury or water and weigh it ; these cases will be dealt with as they occur.

Where it is impossible to introduce mercury or water into the apparatus, air must be used to determine the volume. The apparatus is filled with air under conditions of temperature and pressure which can be determined, and the volume of the air, which is removed by means of a pump (Chap. II.) and carefully collected, is measured in a carefully calibrated gas burette.

## CHAPTER IX

### GAS ANALYSIS

Absorption of gases by solid or liquid reagents—General principles—Methods of manipulation, apparatus, etc. — Oxygen — Hydrogen — Carbon dioxide — Carbon monoxide— Ethylene—Acetylene—Estimation of benzene—Combustion of gases.

THE most convenient method by which the composition of a gaseous mixture can be determined consists in the successive absorption of its constituents. The absorbents may be either solids or liquids with which the gases react chemically or physically. The quantity of any particular constituent can be determined either by measuring the decrease in volume produced by treating the mixture with excess of the reagent, or by bringing a known volume of the mixture into contact with a measured quantity of the reagent, and determining the amount of it which has undergone change. The subject will first be considered generally.

Suppose that in a gaseous mixture it is necessary to determine the quantity of one constituent, A. The gas, after being measured, is brought into intimate contact with a reagent which absorbs this constituent, and the unabsorbed gas is again measured. Now if the gas A, which has been absorbed, forms a compound with the reagent so stable that its dissociation pressure approaches zero at the temperature of the experiment, the residual gas may be considered as quite free from it, provided that excess of the absorbent were present, and that sufficient time were allowed for the reaction to become complete. If, on the other hand, as in the case of the absorption of carbon monoxide by cuprous chloride, an unstable compound is formed, it will be necessary to treat the mixture more than once with fresh quantities of the reagent, in order to completely remove the constituent which is undergoing absorption.

When using liquid reagents a source of error presents itself which is almost absent when solid reagents are used. When a mixture of gases is brought into contact with any liquid the constituents are dissolved in proportion to their solubilities, and to their partial pressures. Similarly, gases already in solution in the liquid are given off in like proportion. When, therefore, liquid reagents are used, the change of volume of the gas may be greater or less than the volume of the constituent which the reagent is intended to absorb. This source of error may be eliminated by bringing the reagent in contact with a gas of similar composition to that which it is intended to analyse. The error would disappear if the same reagent were being used for a number of similar analyses, but would be increased if it were necessary to treat the gas repeatedly with fresh quantities of the reagent.

Sometimes the gas is exposed to the action of liquids or solutions on the surface of porous substances such as coke balls. This method may, however, lead to the introduction of traces of air.

The use of solid reagents, or of solid reagents in contact with a thin layer of liquid, leads undoubtedly to the most accurate results in the analyses of gaseous mixtures. The number of solid reagents which can be used is, however, limited, and the operations involved are as a rule more difficult to conduct.

*Methods of manipulation, apparatus, etc.*— Unless a large number of analyses are to be made, it is hardly worth while employing gas pipettes permanently filled with the reagents. For occasional analyses the gas under examination may be treated with the various reagents contained in glass tubes over mercury. A tube is filled with mercury, and a small quantity of a liquid reagent is introduced into it by means of a glass pipette with a curved point. The tube is then brought over the syphon of the measuring burette, and the gas previously measured is allowed to bubble through the mercury and layer of the reagent, and to fill the top of the tube. The measuring burette is then raised in its clamp so that the point of the syphon is clearly seen above the surface of the reagent in the tube, the reservoir of the burette is lowered, the tap is opened, and the gas is drawn out of the tube.

In order to avoid introducing the reagent into the burette it

is necessary to take great care, when withdrawing the gas from the tube, that no liquid enters the capillary syphon. When nearly all the gas has been drawn into the burette the tap should be almost closed, to make it possible to check the flow at the moment that the last trace has been drawn over. The point of the burette should then be brought beneath the surface of the mercury, either by lowering the burette or by lifting the tube, and mercury should be drawn into the capillary to the fiducial mark.

It is practically impossible to regulate the flow of gas into the burette by adjusting the height of the mercury reservoir. It is found far more convenient to lower the reservoir fully, and to regulate the flow of gas by means of the stopcock. Much time and trouble may be saved by employing a second syphon burette in separating the gas from the reagents. The gas is transferred in a clean tube to the measuring burette, which is thus kept free from the reagents.

In this way it is possible to treat gases with reagents such as caustic soda, sulphuric acid, ammoniacal cuprous chloride, with other reagents which do not attack the mercury, or even with fuming sulphuric acid.

The Oettel gas pipette and its modifications are more suited to the purpose of commercial gas analysis, and have been fully described by Hempel and others.

A convenient form of gas pipette for use with either solid or liquid reagents is shown in Fig. 65. By means of a two-way millimetre-bore stopcock the tube *a* may be placed in communication either with the interior of the pipette or with the open thistle-head funnel *b*. The tube *a* can be directly connected with the measuring burette, or with a second burette, as already described, by means of a piece of thick-walled rubber tube, and the pipette can be conveniently supported by means of a clamp.

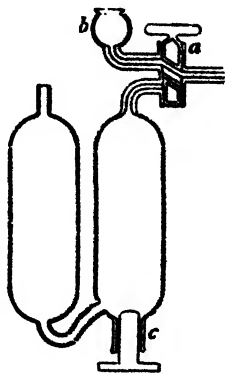


FIG. 65.

The pipette is first filled with the reagent, or with the reagent over mercury, a small quantity of mercury is placed in the funnel *b*, and the tap is turned so that the mercury flows into the tube *a*, expelling any



trace of the reagent. The pipette is then connected with the measuring burette, and the gas is allowed to flow into it and to stand in contact with the reagent for as long a time as is necessary for complete absorption; the liquid is partially expelled into the open part of the pipette. The gas is then drawn back into the measuring burette, the liquid being allowed to rise in the pipette till it just fills the passage in the plug of the stopcock. The gas which remains in the connecting tubes is drawn into the burette by turning the stopcock so that a little of the mercury in *b* flows into *a*.

In order to expose a greater surface of liquid to the gas the pipette may be packed with vertical glass tubes.

If the pipette is used with a solid reagent in presence of water or mercury, the solid is introduced in sticks through the opening *c*. The opening may be conveniently closed by a glass stopper of smaller diameter covered with a piece of rubber tube. Ground stoppers often become fast and cannot be removed without breaking the pipette.

If the reagent is likely to deteriorate by contact with the air the opening in the second chamber may be closed by means of a rubber balloon, and the chamber filled with hydrogen or some inactive gas. The gas expelled from the chamber by the rising liquid passes into the balloon. Rubber balloons cannot be used in the case of fuming sulphuric acid or other corrosive liquids.

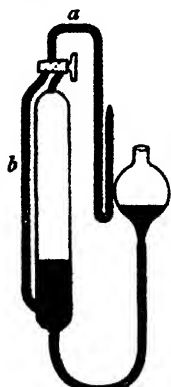


FIG. 66.

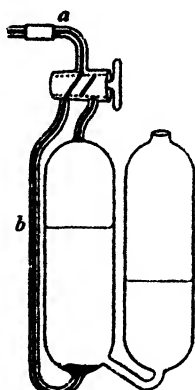


FIG. 67.

Another form of gas pipette (Figs. 66 and 67) possesses the additional advantage that the gas which enters it passes through the reagent and does not merely come into contact with its surface. In this instrument, which may be used in connection with a gas burette (Fig. 67), or which may be constructed so that it may be used independently (Fig.

66), the tube *a* is connected at will through the stopcock either with the top of the pipette, or with a tube *b* which reaches to

its lower end. The pipette must contain sufficient mercury to cover the opening of *b*.

The gas is introduced into the pipette by placing *a* and *b* in communication, and adjusting the pressure so that the gas rises in bubbles through the reagent. When the gas is expelled from the pipette, the stopcock is turned in the opposite direction and the liquid allowed to rise till it fills the passage in the tap; the connecting tubes are cleared by means of mercury drawn up through *b*.

*Absorption of gases by solid or liquid reagents*

**OXYGEN**—*By potassium pyrogallate*.—This method should not be employed if the residual gas is intended for spectroscopic examination, since small quantities of carbon monoxide are always evolved. Hempel recommends that a solution of the following composition should be used:—A solution containing 5 gm. of pyrogallol in 15 c.c. of water is mixed with 120 gm. of caustic potash dissolved in 80 c.c. of water; the liquids should, if possible, be mixed in the pipette.<sup>1</sup> Stronger solutions evolve carbon monoxide in presence of oxygen.

*By phosphorus in the cold*.—A pipette (Fig. 65) is filled with thin sticks of phosphorus and water. The gas is run in and allowed to stand for a few minutes when the whole of the oxygen will be absorbed. The pipette must be painted black on the outside, otherwise the phosphorus will become coated with the amorphous variety owing to the action of light. This is the safest method for the absorption of oxygen in the analysis of a gaseous mixture. The presence of hydrocarbons, sulphuretted hydrogen, etc., appear to interfere with the oxidation of the phosphorus.

*By phosphorus vapour*.—Small quantities of gas may be conveniently treated in the following manner:—A small piece of phosphorus is dried, rubbed between the fingers below the surface of the mercury in a trough, and introduced into a dry gas-tube previously filled with mercury. The tube is then warmed, and the phosphorus which rises to the top melts and adheres to the glass. The gas is next introduced from the burette, and the phosphorus vapourised by warming the tube with a Bunsen burner; the

<sup>1</sup> Clowes (*B. A. Report*, 1896, 747) finds that a solution of 10 grams of pyrogallol and 160 gms. of caustic potash in 200 c.c. of water gives practically no carbon monoxide.

whole of the oxygen is immediately absorbed, and the water is at the same time removed through the formation of phosphorous and phosphoric acids. If the gas contains much oxygen, only a few cubic centimetres should be introduced before the phosphorus is again warmed; the remaining gas is then allowed to run into the tube sufficiently slowly to prevent the combination becoming too violent. This method cannot, of course, be used if the gas contains  $H_2$ , CO, etc. Care must be taken that the point of the syphon of the burette does not come in contact with the melted phosphorus, or it will become plugged.

Globules of yellow phosphorus for this purpose may be made by melting the solid below water in a test-tube, drawing it into a pipette, and allowing it to flow in a stream into a deep cylinder filled with cold water.

*Metallic copper.*—Von Jolly (*Wiedemann's Annalen*, N.F., vi. 520), in his determinations of the composition of air, used a spiral of copper wire heated by means of an electric current for the absorption of the oxygen. The method is not, however, easy to apply.

If a gas consists almost entirely of oxygen, and contains a small residue which it is intended to examine spectroscopically, the oxygen is conveniently removed by heated copper. A hard glass tube closed at one end and filled with reduced copper oxide is attached to the apparatus employed for the absorption of nitrogen by calcium (Fig. 70, p. 102). The gas is introduced into the burette, allowed to flow into the heated tube, which is previously exhausted, and finally collected through the pump.

*By metallic copper in contact with an alkaline solution.*—Hempel has shown that copper gauze in contact with a solution containing equal parts of ammonia solution (880), and water saturated with ammonium carbonate, absorbs oxygen with great rapidity. The gauze is packed in rolls into a pipette (Fig. 65) which is filled with the solution. This method cannot be used in presence of carbon monoxide and acetylene, which are also absorbed.

Ferrous and chromous hydrates have been used as absorbents for oxygen, but they appear to possess no particular advantages.

**HYDROGEN.**—No liquid absorbent is known by means of which hydrogen may be removed from a gaseous mixture. Hempel states that hydrogen may be separated from a mixture of gases

by direct absorption by spongy palladium, obtained by heating its double chloride.

Since, however, spongy palladium loses practically the whole of its hydrogen at the ordinary temperature of the air when placed *in vacuo*, it would seem impossible that this method could give accurate results. Indeed, it was found that when an attempt was made to remove the hydrogen from helium only part of the gas was absorbed.

*By lithium.*—See p. 103.

*By sodium or potassium.*—The absorption of hydrogen by sodium and potassium was investigated by Troost and Hautefeuille (see p. 42). Jaquelain attempted to apply the method to the separation of hydrogen from hydrocarbons, etc. (*An. Ch. Ph.* 74, 203.) It is not, however, very satisfactory in its application.

**CARBON DIOXIDE.**—This gas may be removed from a mixture by absorption, by means of a solution of caustic potash, or by means of solid potash placed in a burette for solid reagents.

*Carbon dioxide in air.*—(A monograph on this subject by Letts and Blake, *Dublin Royal Society*, 1899, 1900, contains very full information.) The method usually employed for the estimation of carbon dioxide in air consists in absorbing the gas contained in a known volume of air by a standard solution of barium hydroxide, and titrating the excess of alkali with oxalic acid. This method, first rendered practical by Pettenkofer, has been modified by Winckler, Hesse, and others.

Since barium hydroxide attacks the glass vessels in which the operations are conducted, and in which the standard solution is stored, they should be coated internally with a thin layer of paraffin wax. This may easily be done by pouring the melted wax into the bottle which has previously been warmed, and allowing the excess of wax to drain out. It might also be as well to coat the inside of the pipettes which are used in the analysis; this, however, would involve the necessity of redetermining their volumes.

The following solutions are required:—

(a) A solution containing 5.6325 gm. of pure crystallised oxalic acid in one litre of water; 1 c.c. of solution is equivalent to 1 c.c. of carbon dioxide.

(b) Stock baryta solution containing 1000 gm. of barium hydrate, and 50 gm. of barium chloride in 5 litres of water.

(c) Dilute baryta solution obtained by adding 30 c.c. of the strong solution to 1 litre of water. These solutions should be kept in large bottles, and drawn off by means of a syphon passing through the cork; air is admitted to the bottle through a tube containing soda lime.

(d) A solution containing 1 gm. of phenol phthalein in 250 c.c. of water.

The strength of the baryta solution is determined by running into a small flask from a burette nearly sufficient oxalic acid solution to neutralise a known quantity (10 or 25 c.c.) of the baryta solution. The baryta solution is then added from a pipette, phenol phthalein solution is added, and the oxalic acid is run in till the neutral point is reached. It is, perhaps, more convenient to add the indicator directly to the baryta solution in the bottle. In this, and in all subsequent titrations, the phenol phthalein should be added from a roughly graduated pipette. The amount of the indicator added should be proportional to the quantity of solution used.

The carbon dioxide in air can be estimated by running a quantity of baryta solution from a pipette into a large glass vessel of known capacity, waxed inside, and fitted with a ground glass or rubber stopper. After thoroughly shaking, the excess of baryta is titrated with oxalic acid.

This method is not very accurate, since when the stopper is removed, fresh air, containing carbon dioxide, enters by diffusion. W. Hun has modified the process in such a manner as to eliminate this source of error.

Thick-walled Erlenmeyer flasks, varying in capacity from 500 c.c. to 60 c.c., are fitted with two-hole rubber stoppers; the holes are closed by pieces of glass rod. The capacities of each of the flasks, up to a mark on the neck to which the stopper fits, should be determined. A 10 c.c. pipette, and a burette made sufficiently long below the tap to pass through the stoppers of the conical flasks are also required.

Air is drawn through one of the flasks by means of a suction bellows (p. 35), and a quantity of baryta solution is introduced by inserting the point of the pipette, filled with the solution, into one of the holes in the stopper of one of the flasks. The glass rod is slightly withdrawn from the second hole to allow air to escape; it is then again inserted, the final drop of solution is

expelled from the pipette by closing the upper end of it with the finger and warming it with the hand; the pipette is then withdrawn, and the second hole is plugged.

After thoroughly shaking, the point of the burette, which contains the oxalic acid solution, is introduced in the same manner, and the acid solution is run in till the colour disappears.

The difference between the titre of the baryta solution added, and the quantity of oxalic acid solution used, give the volume of carbon dioxide in cubic centimetres. The volume of the flask, less 10 c.c., gives the volume of air used.

Carbon dioxide has also been determined gravimetrically by passing a large volume of air, dried by passage through tubes containing sulphuric acid and pumice, through bulbs containing a solution of caustic potash.

**CARBON MONOXIDE.** *By ammoniacal cuprous chloride.*—The solution is prepared as follows:—28 gms. of copper oxide, dissolved in about 500 c.c. of concentrated hydrochloric acid, is allowed to stand in a flask filled with copper turnings till the solution has lost its colour. The solution is then poured into an inverted bell-jar filled with water; the cuprous chloride is allowed to settle, and the liquid is run off by drawing down the glass tube, which passes through the cork, to the level of the precipitate. The precipitate is washed with water, run into a 500 c.c. flask with about 300 c.c. of water, and ammonia passed into it till the precipitate dissolves. The air may be excluded by passing  $\text{CO}_2$  into the flask from a Kipp's apparatus. The solution is finally made up to 500 c.c. with boiled water.

Since the product, which is probably a direct compound of the type  $\text{Cu}_2\text{Cl}_2\text{nCO}$ , is very unstable (*C. r.*, 1899, **128**, 114), the gas must be treated more than once with the ammoniacal cuprous chloride solution to eliminate the whole of the carbon monoxide. It is usual to employ two pipettes, one of which contains a solution which has been used many times, the other containing a fresh solution. The solution must be protected from the air in the open limb of the pipette. The pipette may be packed with copper gauze. *Acid cuprous chloride* does not seem to be such an efficient absorbent as the alkaline solution, and as it reacts with mercury it is difficult to manipulate.

It must be remembered that acetylene also combines with

ammoniacal cuprous chloride to form the red compound  $\text{Cu}_2\text{Cl}_2$ ; this can, however, be immediately recognised. According to Hempel, ethylene is also very soluble in this reagent.

*The detection and estimation of small quantities of carbon monoxide in air* (*J. Physiol.*, 1895, xviii. 461, *Brit. Ass. Report*, 1895). Haemoglobin, the colouring matter of blood, forms addition compounds both with oxygen and with carbon monoxide. Both compounds dissociate easily, but the carbonic oxide derivative is much the more stable of the two. In presence of both oxygen and carbon monoxide the haemoglobin distributes itself between the two gases: the ratio between the amounts of oxyhaemoglobin and carboxyhaemoglobin being equivalent to the ratio of the partial pressures of the gases in the mixture, multiplied by a constant. The percentage of oxygen in air, or other gaseous mixtures, can easily be determined, and, if the value of the constant is known, the quantity of carbon monoxide can be calculated after finding the relation between the quantities of oxyhaemoglobin and carboxyhaemoglobin in a solution of blood which has been in contact with the gas.

Taking advantage of the fact that a dilute solution of oxyhaemoglobin has a yellow colour, while a solution of carboxyhaemoglobin is pink, it is easy to determine, by a colorimetric method, the proportions in which these substances are present. The following solutions are required:—

A 5 per cent solution of defibrinated ox blood. The blood may be kept in a corked bottle; the solution must be prepared fresh.

A solution of carmine. One gram of carmine is mixed with a few drops of ammonia in a mortar, and dissolved in 100 c.c. of glycerine. Ten cubic centimetres, diluted to one litre with water, forms the standard solution.

The air to be examined is drawn through a flask of about 200 c.c. capacity, fitted with a well-paraffined cork, through which pass two glass tubes, which can be closed by means of rubber tubes and stoppers. About 5 c.c. of the blood solution is drawn into a pipette, the point of which is introduced into one of the rubber tubes from which the stopper is removed, air being allowed to escape from the flask by loosening the second stopper. The pipette is then withdrawn, the opening closed, and the flask shaken very gently for about five minutes.

The liquid is then transferred to one of three test-tubes of exactly the same diameter. In another of the test-tubes 5 c.c. of the original blood solution is placed, and in the third the same quantity of the blood solution which has been saturated with carbon monoxide by shaking with coal gas.

Standard carmine solution is now added from a burette to the second test-tube, till the tint of the liquid is the same as that of the solution which has been saturated with carbon monoxide, and to the liquid in the first test-tube till the same tint is produced.

If  $x$  c.c. were added in the first case, and  $y$  c.c. in the second, we have

$$\frac{y}{y+5} \times \frac{x+5}{x} \times 100 = S,$$

where  $S$  is the percentage saturation of the blood shaken with air containing carbon monoxide.

The quantities of carbon monoxide in the air may be calculated from the following table:—

Percentage saturation.	Carbon monoxide in air.
10	0·015 per cent.
20	0·04    "
30	0·08    "
40	0·12    "
50	0·16    "
60	0·22    "
70	0·30    "
80	0·60    "
90	1·2     "

The method gives fairly accurate results for quantities of carbon monoxide in air between 0·015 and 1 per cent. If greater quantities are present the gas must be diluted with air.

The only obvious source of error in the process might be due to the absorption of the carbon monoxide by the reagent, and consequent decrease of its partial pressure in the mixture. The quantity of the gas which is absorbed by the hæmoglobin is, however, too small to come within the limits of experiment.

Dr. Haldane has also investigated the dissociation pressure of carboxyhæmoglobin (*J. Physiol.* xviii. 453).

Vogel (*Ber.* 10, 792; 11, 235) was the first to make use of the hæmoglobin method for the detection of carbon monoxide,



but he was unable to detect the gas in a mixture containing less than 0.25 per cent of it.

The reduction of iodic anhydride by carbon monoxide has been employed by Nicloux (*C. r.*, 1898, **126**, 746), and Gautier (*C. r.*, 1898, **126**, 931) in estimating the quantity of it in air.

**HYDROCARBONS.**—Qualitative tests for hydrocarbons, etc. (Philips, *Ann. Ch. J.* **16**, 255):

(i) Solutions of palladium chloride are reduced by carbon monoxide, with formation of carbon dioxide: the latter is not formed in the case of olefines.

(ii) Ammoniacal silver nitrate gives a yellow precipitate with acetylene, but is not altered by olefines; carbon monoxide reduces it, producing metallic silver.

(iii) Platinum chloride yields carbon dioxide with carbon monoxide, but it is not immediately reduced to metal: ethylene produces no change.

ETHYLENE may be absorbed from a mixture of gases, either by fuming sulphuric acid or by bromine water.

If *fuming sulphuric acid* is used, it should contain about 10 per cent of sulphur trioxide. The acid should be contained in a pipette for liquid reagents (Fig. 65), and its exposed surface should be protected from the air while not in use. After treatment with fuming sulphuric acid the gas must be passed into a pipette containing caustic potash, to absorb the acid fumes.

It must not be forgotten that fuming sulphuric acid absorbs not only the ethylene hydrocarbons, but also acetylene, and the vapours of aromatic hydrocarbons such as benzene.

*Bromine water* is equally efficient as an absorbent for hydrocarbons of the ethylene series, and does not absorb the vapours of the aromatic hydrocarbons to such an extent. Since bromine reacts very rapidly with mercury, it is necessary to employ a

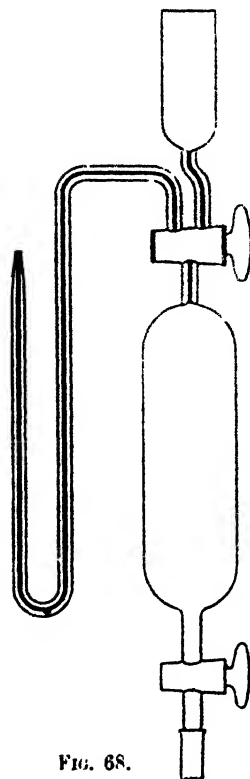


FIG. 68.

specially constructed pipette (Fig. 68). The gas is drawn into the

pipette and the pressure is lowered till the mercury falls below the lower stopcock, which is then closed. Excess of bromine water, or, if much ethylene is present, of bromine, is poured into the cup connected with the upper stopcock, and run into the pipette; after shaking, potash is run into the pipette, and the gas is transferred to a tube, and afterwards to the measuring burette.

ACETYLENE (Preparation, see p. 53).—Although acetylene can be directly absorbed by fuming sulphuric acid, or by bromine water, it is not usually convenient to use these reagents for its estimation, since they also take up ethylene, etc. When alkaline solutions of certain mercuric, cuprous, or silver salts are shaken with acetylene, the whole of the gas is absorbed, and insoluble metallic acetylides are formed. The cuprous acetylide,  $\text{Cu}_2\text{C}_2\frac{1}{3}\text{H}_2\text{O}$ , obtained by shaking acetylene with ammoniacal cuprous chloride, is a red compound, is somewhat explosive, appears to decompose in presence of air and water, and is easily decomposed by hydrochloric acid (see p. 53). The silver acetylide is a yellow compound: it is too explosive to be handled with safety. The mercuric acetylide (*Ch. Soc. J.*, 1894, 262),  $\text{HgC}_2\frac{1}{3}\text{H}_2\text{O}$ , is white; it cannot be obtained pure by the action of acetylene on ammoniacal solution of the chloride, cyanide, etc., but is most easily obtained by the use of a reagent prepared in the following manner:

Freshly precipitated mercuric oxide is washed free from potash, and treated with ammonia (880) and solid ammonium carbonate in powder. The solution is filtered, and may be kept in a stoppered bottle for use. In order to absorb the acetylene a small quantity of the reagent is placed in a bottle furnished with a rubber stopper, with a stopcock passing through it. The bottle is exhausted and attached by a rubber tube to the burette containing the gas. The gas is drawn directly into the bottle, and in order to clear the leading tubes successive small quantities of air are admitted into the burette. After shaking thoroughly, the precipitated acetylide is filtered off, washed with ammonia solution, treated in a beaker with dilute ammonium sulphide, and weighed as sulphide.

BENZENE AND HIGHER HYDROCARBONS.—Berthelot's method of absorbing the hydrocarbons,  $\text{C}_n\text{H}_{2n}$ , with bromine, and the benzene hydrocarbons with fuming nitric acid, is of no use, as the bromine attacks the benzene. A method by which the benzene is esti-

mated as dinitro-benzene has, however, been found to yield good results (*Zeit. Anorg. Ch.* 1898).

Bunsen passed the gas through several tubes filled with absolute alcohol in order to absorb the hydrocarbons. The oil which separated when the alcohol was poured into brine was collected and analysed.

St. Claire-Deville separated the hydrocarbons by passing the gas through a spiral cooled to  $-22^{\circ}\text{C}$ . The temperature is not, however, low enough to condense the whole of the vapour. A mixture of solid carbonic acid and ether appears to condense a very large quantity of vapour out of coal gas: liquid air gives a similar result. The liquid consists mainly of benzene and water, and it is found that unless the tube through which the gas enters the condenser is made very wide, it becomes plugged almost directly.

COMBUSTION OF GASES.—In many cases the only possible method of analysing a gaseous mixture consists in determining the nature of the changes which it undergoes during combustion.

The combustion of the gas, mixed either with excess of oxygen, air, or hydrogen, is usually accomplished by exploding the mixture by means of an electric spark from an induction coil, or by passing it through a tube containing spongy palladium.

*Combustion by explosion.*—The explosion pipette can be made conveniently of the same form as the measuring pipette for analysis at constant pressure, but it should be of stouter glass, and should have two platinum wires sealed into it close to the top. The gas is introduced, and exploded by means of a small coil, capable of giving a quarter-inch spark, and a dip battery or small accumulator cell. The gas may be exploded under reduced pressure by lowering the mercury reservoir, and to prevent accidents the apparatus may be covered with a cloth during the experiment.

Considerable errors may be introduced through the combustion of the grease with which the stopcock is lubricated; it is therefore advisable to employ metaphosphoric acid for this purpose.

By combustion of a gaseous mixture by explosion we can obtain the following data:—

1. The total contraction.
2. The carbon dioxide formed by the combustion.

3. The total oxygen used in the combustion.

4. The volume of nitrogen, argon, helium, etc., remaining over.

Under certain conditions some of the nitrogen enters into combustion with the oxygen. Bunsen found that in presence of excess of combustible gas nitrogen was oxidised with formation of nitrous and nitric acids. When quantities of oxyhydrogen gas up to 64 volumes were burned in presence of 100 volumes of air, the quantity of nitrogen oxidised was practically negligible, but with higher proportions of combustible gas the error became considerable. It is, therefore, preferable to use air, or air and oxygen, instead of pure oxygen in the case of combustible gases which contain but a small proportion of nitrogen.

On the other hand, there is a danger of introducing a considerable error owing to incomplete combustion of the gas, either owing to there being insufficient oxygen present, or to too great dilution with incombustible gas. This first condition may, in the case of methane or ethylene, lead to the formation of carbon monoxide, but this may easily be avoided by taking care that sufficient oxygen is added before the explosion. The second difficulty may be overcome by adding sufficient electrolytic gas to the mixture; the quantity need not be accurately measured as it does not appear in the final calculation.

Limiting values of explosive mixture of gases with air:—

Acetylene . . . . .	3 - 82 per cent.
Hydrogen . . . . .	5 - 72 „
Carbon monoxide . . . . .	13 - 75 „
Ethylene . . . . .	4 - 22 „
Methane . . . . .	5 - 13

**HYDROGEN.**—This gas may be directly estimated in absence of carbon monoxide, hydrocarbons, etc., by exploding it with rather more than half its volume of oxygen. If much inactive gas is present it is necessary either to add electrolytic gas, to pass the gas over palladium, or to pass the spark through it for some minutes; in the latter case the oxygen may enter into combination with some of the nitrogen which is present. The error due to incomplete combustion is small, and for electrolytic gas is not greater than 0001 of the whole. Since, however, the volume relation of oxygen to hydrogen in electrolytic gas is probably

1 to 2.003 an error of one part in a thousand is incurred by considering it to be 1 to 2.

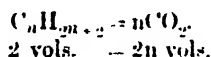
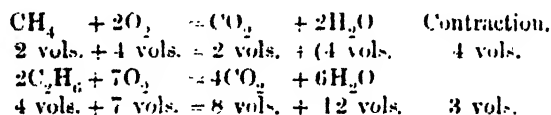
**CARBON MONOXIDE.**—Since the volume of carbon dioxide produced by the combustion of carbon monoxide is equal to the original volume of the gas, it is in absence of hydrocarbons easy to determine the quantity of carbon monoxide present.

Even in presence of excess of oxygen the combustion is never quite complete, a small trace of the gas is always left uncombined; and, if it is intended to examine the residue spectroscopically, it should be sparked (p. 104) before the oxygen is absorbed. The quantity of carbon monoxide left uncombined is too small to affect the analysis.

**CARBON MONOXIDE AND HYDROGEN.**—From the data obtained by exploding the gas with oxygen the quantity of these gases may be calculated in absence of hydrocarbons.

Vol. of hydrogen =  $\frac{2}{3}$  total contraction -  $\frac{1}{2}$  vol. of carbon dioxide formed

**PARAFFIN HYDROCARBONS.**—The following equations represent the changes which take place when the paraffin hydrocarbons are burnt with oxygen:—



From these results it is clear that it would be possible to determine the nature of the hydrocarbon, provided that no hydrogen or carbon monoxide were present.

In most cases it can be assumed that the paraffin hydrocarbon present is entirely methane. From the first equation the volume of carbon dioxide formed should be equal to the volume of the methane, and consequently, to half the total contraction or to twice the quantity of oxygen consumed. If this is not the case other combustible gases must be present. If the quantity of oxygen consumed is too great, hydrogen must be present; the formation of too much carbon dioxide indicates the presence of carbon monoxide or higher hydrocarbons.

Hydrocarbons may be separated by fractional distillation (Ch. xvi.)

**HYDROGEN AND METHANE.**—The quantity of hydrogen and methane, in absence of higher hydrocarbons, olefines, or carbon monoxide, can be estimated by direct explosion with oxygen.

Vol. of carbon dioxide = vol. of methane.

Vol. of hydrogen =  $\frac{2}{3}$  (total contraction - 2 vols. of methane).

**HYDROGEN, CARBON MONOXIDE, AND METHANE.**—The quantities of these three gases present in a mixture is sometimes determined by calculation from data obtained from combustion of the mixture with oxygen. The process involves the use of three simultaneous equations, and unless the co-efficients (the actual observed results) are obtained with very great accuracy the results are practically valueless.

## CHAPTER X

### THE COMPOSITION OF ATMOSPHERIC AIR

THE first quantitative experiments on the composition of air were made by Priestley, who made use of the reaction between nitric oxide and oxygen, first observed by Mayow, in order to determine the "goodness" of atmospheric air. He did not, however, obtain very good results by this method, but he succeeded in showing by experiments on living mice, that dephlogisticated air (oxygen) was capable of supporting life four or five times as well as ordinary air.

His contemporary Scheele, about the year 1775, showed that about 6 parts out of 20 parts of air were capable of being absorbed by liver of sulphur. Lavoisier, by heating mercury in air, obtained results which varied between 20 and 25 per cent of oxygen.

The first accurate experiments were made by Cavendish in the year 1781. He employed the method suggested by Volta of exploding the air with hydrogen, and obtained as the mean of several determinations the number 20.85. The result is worthy of this admirable experimentalist.

Dalton, who may be said to have partly based his atomic theory on his observations with regard to the action of nitric oxide on air, obtained results which are far from accurate, ranging between 19.8 and 21.1 per cent of oxygen.

In 1804 Gay-Lussac analysed a large number of samples of air brought from different parts of the world by von Humboldt. The results, which vary between 21.1 and 20.9 per cent of oxygen, show that the composition of air is practically constant all over the earth's surface. Neither the results of Gay-Lussac, of Davy, nor of Bunsen exceed in accuracy those of Cavendish.

In recent years careful analyses have been made by Kreusler, Morley, Hempel, Oettel, and others, to determine within what limits the quantity of oxygen in the air may vary. The methods employed are described in Hempel's book on gas analysis; the results of analyses of the air of Munich are briefly as follows:—

Kreusler, Oct.	27, 10 experiments,	20·906	per cent of oxygen.
"	" 18, 6 ..	20·916	" "
"	July 25, 10 ..	20·912	" "
Oettel	April 5, 4 ..	20·938	" "

Von Joly found that the composition of the air of Munich varied with the direction of the wind, and Lewy (*C. r.*, **31**, 725; **33**, 345; **34**, 5) found that the air near the Ganges swamps contained only 20·4 per cent of oxygen.

Leduc (*An. de Ch.*, 1898, 18) has employed a gravimetric method for the analysis of air. Several sticks of phosphorus were introduced into a glass globe, which was then exhausted and weighed. Dry air was then admitted, the globe was weighed, and, after allowing sufficient time for the complete absorption of the oxygen, it was exhausted and weighed again. The results indicate that the quantity of oxygen in the air varies according to locality, distance from the soil, etc., over about 0·1 per cent.

It appears that the air in wells and quarries in limestone districts varies considerably with internal atmospheric conditions. It is probable that with a rising barometer the air is forced into the porous rocks, oxidising carbonaceous matter and taking up carbon dioxide from bicarbonates. When the pressure falls the air escapes charged with carbon dioxide, and since the rate of diffusion of the latter is considerably lower than that of air, it remains in the lower strata, and finds its way in considerable quantity into mines and quarries.

The quantity of carbon dioxide in air varies between 3 parts per 10,000 over the open sea to 3 parts per 1000 in a crowded room. Ammonia is present to the extent of less than 1 part per 10,000 parts of air. Gautier has shown that hydrogen is present in the air of Paris. The constituents of atmospheric nitrogen will be discussed later.

Though the composition of air does not, under favourable conditions, vary between very wide limits, it is obvious that it should not be used as the standard for comparative physical



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measurements when any high degree of accuracy is desired. It appears, however, that the quantity of the inactive gases in atmospheric nitrogen remains constant; and as this gas is very easily obtained, it might well be employed as an empirical standard.

## CHAPTER XI

### THE GASES OF THE HELIUM GROUP

The discovery of argon—Methods of obtaining argon—Separation of the inactive gases from nitrogen, etc.—Preparation of argon in large quantity—Helium—The rare gases.

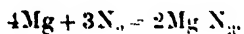
THE discovery of argon in 1894 by Lord Rayleigh and Professor Ramsay, in indicating the probable existence of a class of elementary substances apparently devoid of chemical properties, opened up an entirely new field of investigation. The history of the discovery of argon has been detailed by Professor Ramsay in his well-known work *The Gases of the Atmosphere*, and it is only necessary to recall here the researches on which the discovery was based.

In 1785 Cavendish had shown that when sparks from an electrical machine were passed through air contained over mercury in an inverted U-tube in presence of potash, nitre was produced. If, when no further contraction took place in the volume of the gas, more dephlogisticated air (oxygen) were added and the sparking continued, there still remained, after absorption of the oxygen with liver of sulphur, a small quantity of gas. The volume of this gas, which was  $\frac{1}{120}$  of the volume of the air taken, did not diminish on further sparking with oxygen.

Cavendish's experiment appears to have been entirely overlooked; but in 1894 Lord Rayleigh's discovery that the density of atmospheric nitrogen was about half of one per cent higher than that of nitrogen from chemical sources, gave fresh indication of the existence in air of some hitherto undiscovered gas. The investigation of the cause of this anomaly carried out conjointly with Professor Ramsay led to the discovery of argon.

It had long been known that when metallic magnesium was burnt in air it entered into combination with the nitrogen as

well as with the oxygen, forming a mixture of the oxide and nitride.



This principle was first applied by Ramsay and Rayleigh to the preparation of argon (*Phil. Trans.*, 1895, 187), and although the process which they employed is no longer in use it is of considerable historical interest.

Atmospheric nitrogen, obtained by drawing air over red-hot copper, was passed through a hard glass tube, filled with magnesium shavings and heated in a combustion furnace: the residual gas was collected over water in a gasholder. The progress of the reaction was easily followed by watching the glow in the tube caused by the combustion of the magnesium. When the magnesium was exhausted the gas in the tube was carried over into the gasholder, which now contained nitrogen rich in argon, by a more rapid current of nitrogen. The nitrogen was passed backwards and forwards over magnesium till it was reduced to about one-fortieth of its original bulk.

In order to remove the remaining traces of nitrogen, hydrogen, etc., from the argon, it was circulated for some hours through tubes containing red-hot magnesium and copper oxide, soda-lime and pentoxide of phosphorus. The apparatus employed is shown in Fig. 69.

The gas was contained over mercury in a reservoir A, with two outlets, one at the top and one at the side some little distance from it. The tubes C and B were of hard glass, and contained respectively magnesium turnings and copper oxide partially reduced; the tubes were heated to a dull red heat in small tube-furnaces. The tubes D and E contained soda-lime and pentoxide of phosphorus; the latter served to absorb water vapour, which would otherwise have reacted with the magnesium, producing hydrogen. The gas was made to pass in a continuous stream through the tube and reservoir by means of the apparatus shown on the right-hand of the figure, and first described by Prof. N. Collie (*Chem. Soc. J.*, 1889, 110). Mercury from the reservoir G fell in drops down the capillary tube H into the chamber K, causing a continuous current of the gas to flow in the same direction. The mercury escaped from K through the tap L, which was so regulated that it flowed in a

steady stream into the vessel M, which was connected by a capillary tube N with the tube O, which was partially immersed in the mercury in the reservoir G, and was connected with a water-pump through P. A piece of rusty iron wire, twisted and inserted in the lower opening of the capillary tube, prevented the mercury flowing out of K from completely closing it, so that as soon as the mercury came into contact with the upper lip of the opening it was carried by the air in a shower of minute pellets through the capillary tube into the reservoir G. This process

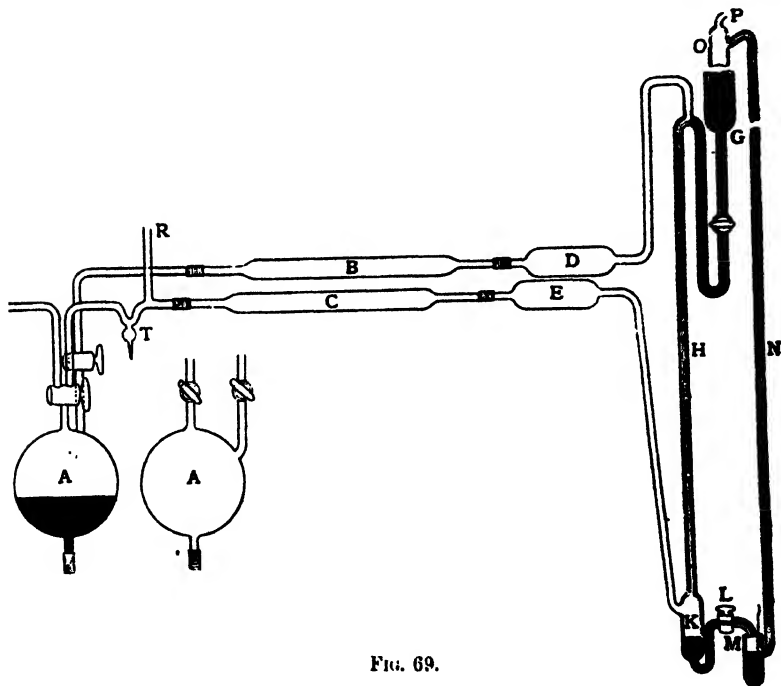


FIG. 69.

would go on continuously for hours without any attention, so long as the iron wire was properly adjusted and the flow of the mercury carefully regulated at the commencement of the experiment.

In order to remove the air originally contained in the tubes, and to recover the argon remaining in them at the end of the experiment, the apparatus was connected with a mercury-pump through the tube R. Before exhausting the apparatus all stop-cocks were closed; the tubes containing the magnesium and copper oxide were then heated, and the exhaustion was continued

until the magnesium ceased to give off gas. The stopcock connected with the pump was then closed, and the stopcock connected with the top of the reservoir was turned so as to admit gas to the apparatus; any trace of mercury contained in the tube was caught in the bulb T. The second stopcock was then opened, the level of the mercury was adjusted, and the circulation was allowed to proceed. It was only necessary to readjust the level of the mercury in the reservoir, or to introduce more gas into it from time to time during the course of the experiment.

Since the tube containing the magnesium almost invariably cracked on cooling, it was necessary to remove the gas from it by closing all the stopcocks and exhausting the apparatus by means of the pump.

**ABSORPTION OF NITROGEN BY MEANS OF CALCIUM.**—Macquenne has shown that when pure lime is heated with magnesium dust calcium is produced, and that this metal absorbs nitrogen with great rapidity. Absorption of the nitrogen by calcium has completely replaced the method of circulation over magnesium as a process for the preparation of small quantities of argon from atmospheric nitrogen, and for purifying the inactive gases generally.

Precipitated chalk is heated on a plate in a muffle furnace for some hours, and is then scraped into a basin and allowed to cool in a desiccator. The lime so obtained is thoroughly mixed with about three-fifths of its weight of magnesium dust by shaking in a stoppered bottle. The lime must be *quite free from carbonate or hydrate*, and the mixture must be kept very dry,

otherwise a serious explosion may occur when it is heated.

A quantity of the mixture is confined between plugs of glass wool in a hard glass tube, which is drawn out at the ends so that it can be connected by means of rubber junctions with the two gas-

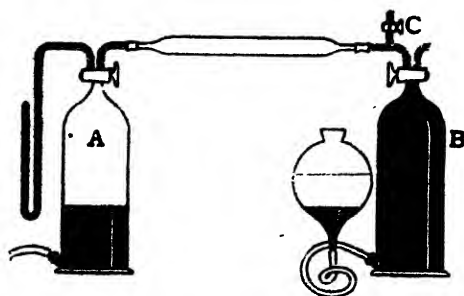


FIG. 70.

holders in the apparatus shown in Fig. 70. The gas to be treated is contained in the gasholder A, and if the quantity of inactive gas

is likely to be small the second gasholder may be dispensed with, and the gas taken directly into the pump through the stopcock C.

The tube is heated to a dull red heat in a tube furnace so long as any quantity of gas can be removed. The evolution of gas, which consists of hydrogen and carbon monoxide, never entirely ceases, but it is easy to remove traces of these gases by passing the gas over heated copper oxide, or better, by sparking it for a short time with oxygen. Before admitting the gas from the reservoir A the tap *e* must be closed; the flow of the gas must be carefully regulated, as the heat generated by the combustion of the calcium is considerable, and there is some danger of melting the tube. After a short time absorption may cease on account of the tube becoming filled with inactive gas. The gas may then be allowed to flow into the gasholder B, or the stopcock leading into A may be closed and the gas removed through the pump. In the latter case the gas in the tube should be allowed to remain in contact with the calcium for a short time before the stopcock C is opened.

A single passage of the gas over the heated calcium is sufficient for the complete absorption of the nitrogen, and the gas may be completely purified by sparking for about five minutes with oxygen. In this way it is possible to demonstrate on the lecture table as a quantitative experiment the preparation of argon from air.

**ABSORPTION OF NITROGEN BY LITHIUM.**—Guntz (*C. r.*, 1896, **123**, 995) has shown that lithium absorbs nitrogen rapidly even at ordinary temperatures. Since, however, the metal attacks glass rapidly below a red heat the application of the method is attended with considerable difficulty.

**SPARKING WITH OXYGEN.**—The discoveries of Priestley and Cavendish have already been referred to, and it remains to describe the practical application of their methods as a means of purifying the inactive gases. In their original investigation of atmospheric air Professor Ramsay and Lord Rayleigh employed a modification of Cavendish's method as a means of obtaining argon, and later Lord Rayleigh obtained about two litres of argon by the same method. In order to save time, however, it is usual to pass the gas over heated calcium, and to employ the method of sparking only as a means of removing the last traces of the active gases.

It is inconvenient to treat more than about 40 c.c. of gas at a time, unless much nitrogen is present. About that quantity of gas is mixed with about 10 c.c. of oxygen in a tube capable of holding 80 c.c. The points between which the sparks are passed are of stout platinum wire fused (Fig. 71) through the ends of glass tubes which are about 5 mm. in diameter, and are bent into a close U, so that the longer limb remains open. The open limbs fit tightly through holes bored in a cork, which keeps them in place. The tubes are filled with mercury, which serves to conduct the current to the platinum points.

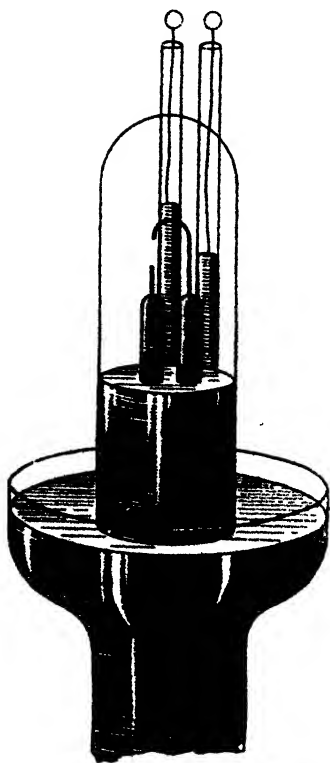


FIG. 71.

On account of the intermittent nature of the discharge from an induction coil, working with a constant current in the primary circuit, one of the points becomes very hot, while the other remains comparatively cool. For this reason one of the wires is made about three times the length of the other, and is bent as in the figure; this point is always made the cathode.

The spark points are introduced into the tube containing the gas while it is standing in a mercury trough (Fig. 28); the tube is held in a screw clamp, and the glass tubes which hold the points are attached to it by a turn of wire so that the points themselves lie near the top of the tube. A small quantity of potash is introduced into the tube through a curved pipette, and the connections made with the terminals of the coil.

An Apps induction coil, giving with four secondary cells a six-inch spark through air, gives very satisfactory results. When, however, it is available the alternating current may be used with effect. The leads from the main are connected with the primary terminals of the coil through an iron wire resistance, so that the current is reduced to about 5 amperes. The contact breaker is then screwed back against the adjustable screw so as to place it

out of action. When working, the coil emits the well-known "transformer hum," and the result is to produce a very hot flame between the spark points. Since in this case there is no polarity in the nature of the secondary discharge both terminals become equally heated.

The sparking is usually continued for three or four hours after contraction has ceased, and, if necessary, more oxygen may be added to the gas as occasion demands. At the end of the operation the spark points are removed, the gas separated from the potash (p. 80), and the oxygen absorbed by means of phosphorus (p. 84).

Lord Rayleigh (*Ch. Soc. Jour.*, 1897, 181) has described a process for the preparation of argon on a large scale by sparking atmospheric air with oxygen.

PRODUCTION OF ARGON ON A LARGE SCALE.-- In the early part of 1898 Professor Ramsay and the author undertook the preparation of 15 litres of argon in order to investigate the homogeneity of that gas. The following account of the process employed is quoted directly from the *Proceedings of the Royal Society* (vol. lxiv. 1898, 183).

In order to prepare 15 litres of argon it is necessary to deal with about 1500 litres of atmospheric air, of which approximately 1200 litres consist of a mixture of nitrogen and argon. To absorb the nitrogen contained in this quantity of gas by conversion into nitride, 4 kilograms of magnesium would be required theoretically, but in order to cover loss through leakage and incomplete action, 5 kilograms of the metal were employed. The absorption of the oxygen and nitrogen was conducted in three stages. In the first, the oxygen was removed by means of metallic copper; in the second, the nitrogen was passed twice over metallic magnesium; and in the third, the gas, now rich in argon, was finally freed from nitrogen and hydrogen by passage over a mixture of anhydrous lime and magnesium powder heated to a red heat, and subsequently over red-hot copper oxide. The apparatus employed is shown in detail in the annexed figure (Fig. 72).

It was, of course, necessary to confine the gas over water between the successive stages of purification, and finally to store the gaseous argon in the same way. On account of the considerable solubility of argon in water, this would have entailed no



small loss if the quantity of water with which it had been brought into contact had been large. We consequently decided to make use of gasholders of the gasometer type, in which the water was contained in an annular space of small capacity. Balance weights were attached to cords passing over pulleys, and served to relieve the pressure on the gas due to the weight of the gasometer. As the volume of the gas decreased after each successive stage, the four gasholders employed were of different sizes: the capacity of A was about 180 litres; that of B, 27 litres; and of C and D, each 18 litres.

Atmospheric nitrogen was obtained by drawing air, freed from carbon dioxide by passage through caustic soda solution, over heated metallic copper. A large iron tube F, 3 feet 6 inches long and 3.5 inches in diameter, containing 25 lbs. of scrap copper, was connected with the gasholder A; the tube was heated in a long fire-brick trough during these experiments, but a gas-furnace, which is shown in the figure, has now been substituted for the more primitive arrangement.

The time required to fill the gasholder was usually about five hours, and it was found, on analysis of the gas, that one single operation sufficed for the complete removal of all oxygen. The oxidised copper was reduced between each operation by means of coal-gas.

By closing the stopcock *b*, and opening the stopcock *c*, the gasholder A could be placed in communication with the apparatus in which the preliminary absorption of nitrogen took place. By placing weights on the top of the gasholder the nitrogen was driven through the vessel M and the U-tube N, both of which contained strong sulphuric acid, into the tube G, which contained magnesium. This tube was a piece of steam-barrel, 1.5 inches in diameter, connected at each end by a reducing socket with an iron tube, 0.25 inch in diameter. The tube contained 250 grams of magnesium, cut into coarse shavings in a shaping machine; the magnesium was not pressed very tightly into the tube. Since after each operation it was necessary to remove the sockets in order to clear the tube, the joints were luted with red lead, and the tube was made of sufficient length to project about 3 inches at each end of the furnace.

The greater part of the nitride was generally removed by

using an iron rod, and the remainder by means of water, which converted it into the hydroxide. The tube was raised to a bright red heat before connecting it with the U-tube O, in order

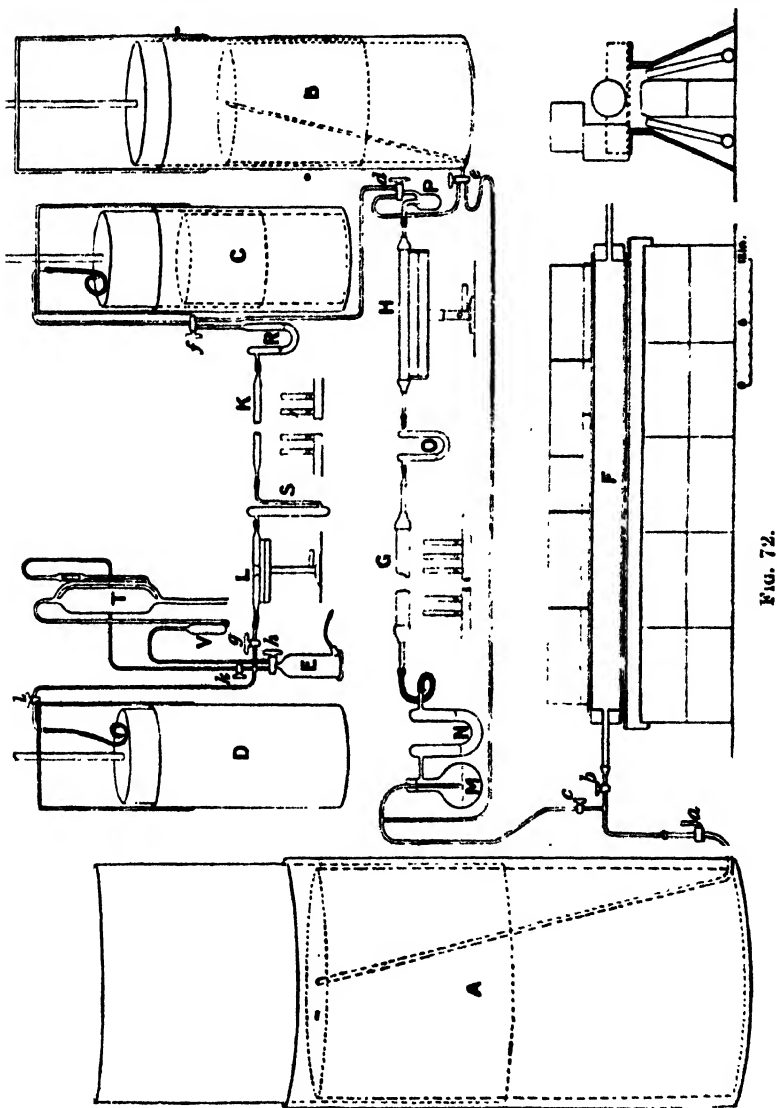


FIG. 72.

to allow the greater part of the hydrogen occluded by the magnesium to escape. The absorption of the nitrogen, which was indicated by the rate of flow of the gas through the U-tubes N and O, was maintained briskly until practically the whole of

the magnesium was converted into nitride; the volume of the gas absorbed was equivalent to half the capacity of the large gasholder.

The gas, after leaving the U-tube O, passed through a second iron tube H containing copper oxide; next, through the vessel P, in which water condensed; and it finally collected in the gasometer B. That which passed during the first stages of the process consisted of nitrogen containing much argon; but towards the end of the operation the argon became much diluted, until finally the gas which passed through the U-tube O consisted almost entirely of atmospheric nitrogen. The tube G was then replaced by another containing a fresh supply of magnesium.

The tap *c* was then closed, and the taps *d* and *e* turned, so that the gas in the gasometer B could be made to flow through the magnesium and copper oxide tubes into the gasometer C. In this process its volume was very much reduced, and the gas which collected in C probably contained as much as 25 per cent of argon. When the whole of the gas had been expelled from B, the taps *d* and *e* were again turned, and atmospheric nitrogen was allowed to flow through the magnesium tube, as in the first stage of this operation.

When the gasometer C had become full of the mixture of nitrogen and argon, as it did at the end of every third or fourth operation, it became necessary to reduce its volume by further absorption of nitrogen. The method employed, which was first described by Maquenne,<sup>1</sup> consisted in passing the gas through a hard glass tube containing a mixture of magnesium powder and lime, heated to a dull red heat in a combustion furnace. The lime was obtained by thoroughly calcining precipitated chalk in a muffle. The nitrogen continued to be completely absorbed as long as calcium remained unattacked, so that the product of this operation consisted of pure argon. The gas issuing from the calcium tube passed through a tube S, containing soda-lime, and over copper oxide in the tube I, on its way to the gasometer D. Since at the end of the operation the system of tubes between the gasholders C and D contained argon, in order to avoid loss, the circuit was placed in communication with a Töpler pump T, through the stopcock *k*. The space between the stopcocks *l* and *f* was exhausted at the commencement of the operation, the

<sup>1</sup> *Comp. rend.*, 1895, 121, 1147.

exhaustion being continued till the greater part of the hydrogen, which is always evolved when a mixture of magnesium and lime is heated, had been given off.

When it was necessary to suspend operations, the taps *l* and *f* were closed, the tap *k* was opened, and the argon was taken into the pump and delivered into the vessel *V* which covered the upturned end of the capillary tube of the pump. From *V* the argon could be drawn into the small gasholder *E*, which contained mercury, and which could also be placed in communication with the system through which the gas passed on its way from *C* to *D*.

These operations were repeated until the gasholder *D* contained about 15 litres of argon.

*Helium*.—In 1889 Hildebrand observed that when certain uranium-containing minerals were boiled with sulphuric acid a quantity of gas was evolved (*Bull. U.S. Geological Survey*, **78**, 83). The gas was supposed to be nitrogen, as its spectrum showed the characteristic fluting, and, consequently, it was not further investigated.

Early in 1895, about three months after the publication of the discovery of argon, Mr. Miers of the British Museum called Prof. Ramsay's attention to Hildebrand's paper, suggesting that the gas might prove to contain argon. A specimen of clévite was obtained and heated with dilute sulphuric acid *in vacuo*; the spectrum of the gas was found to contain the line  $D_3$  ( $\lambda = 5876$ ), observed by Janssen in 1868, and attributed by Lockyer to a solar element of low density to which the latter gave the name helium. This name was retained for the newly discovered gas.<sup>1</sup>

The method of heating the helium-yielding minerals with dilute sulphuric acid in order to obtain the gas is found in practice to be very inconvenient, unless a large quantity of the mineral is to be treated. The mineral must be ground to a very fine powder, and it is necessary to continue the operation for several days in order to completely decompose it, and so obtain the whole of the helium. It was subsequently found that a quantity of the gas was evolved by the action of heat alone, the evolution commencing but slowly at about 200°, and taking

<sup>1</sup> A full account of the properties of helium will be found in a paper by Prof. W. Ramsay (*An. Ch. et de Ph.*, 1898, series vii. 13). A list of the most important papers dealing with this gas is appended.

place rapidly at a bright red heat. It is interesting to note that almost exactly half the helium contained in the mineral is evolved by the action of heat alone (*Proc. Roy. Soc.*, December 1898), and further, that in some cases the evolution of the gas appears to be accompanied by a considerable evolution of heat (*Proc. Roy. Soc.*, January 1898). These facts have been taken to indicate that the helium exists in the minerals, from which it is evolved by the action of heat, in a state of combination. On heating the minerals *in vacuo* the gas appeared to be evolved rapidly at first, particularly in the case of *endothermic* minerals, then more slowly, and finally appeared to cease altogether.

It is probable that the helium is associated in the mineral with a small quantity of argon and perhaps with a trace of nitrogen. In one case only has helium obtained directly from minerals been found to have a density less than 2.18. Langlet (*Zeit. An. Chem.*, **10**, 1895, 819) obtained a sample of density 2.00 by fusing the mineral clévite with acid potassium sulphate; but the gas probably contained hydrogen as it was purified by passage *at low pressure* over heated copper oxide. A separation of pure helium, density 1.98, from the gas obtained by the action of heat on minerals can be accomplished by the method of fractional diffusion, p. 289 (*Proc. Roy. Soc.*, **60**, 206), and by other methods which will be described later.

A number of minerals have been found to yield helium in considerable quantity (*Chem. Soc. Jr.*, 1895, 685; *Proc. Roy. Soc.*, 1898, **64**, 131). The following figures indicate the quantities of the gas obtained, and as clévite can be obtained at about £1 per kilo, the cost is not excessive:—

Mineral.	Locality.	Composition.	Helium in c.c. per gram of mineral.	
			By action of heat.	Sulphuric acid.
Clévite	Sweden	Oxides of uranium and lead, with oxides of rare earths	1.487	3.201
Fergusonite	„	Niobate of yttrium and cerium	1.041	About 2 c.c., but very difficult to decompose

*The preparation of Helium.*—(a) By the action of heat upon minerals.

The mineral is reduced to powder in an iron mortar and passed through a sieve. The apparatus employed is shown in Fig. 73.

The powdered mineral is placed in the tube *a*, which is either of hard glass or iron. If a glass tube is used it is drawn out at the end and connected with the rest of the apparatus by a rubber junction (p. 19), but if the tube is of iron the end is closed by a rubber stopper surrounded by a short water-jacket. The apparatus is connected with a mercury-pump through the stop-cock *d* and with the reservoir *f*: the flask *e* contains sticks of solid potash to absorb water,

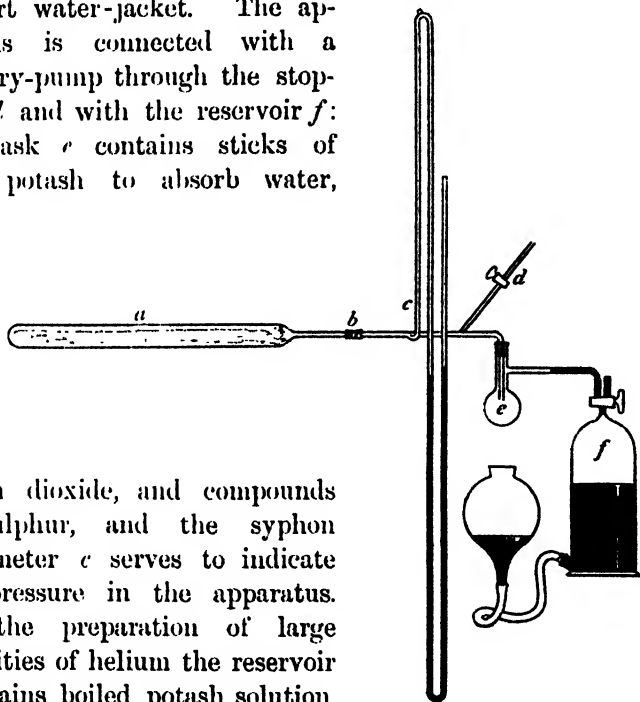


FIG. 73.

carbon dioxide, and compounds of sulphur, and the syphon manometer *c* serves to indicate the pressure in the apparatus. For the preparation of large quantities of helium the reservoir *f* contains boiled potash solution, and when working with small quantities of the mineral a layer of potash is introduced above the mercury in *f*.

After thoroughly exhausting the apparatus the mineral is slowly heated, and as soon as the pressure in the apparatus becomes equal to the atmospheric pressure connection is made with the reservoir *f*. The evolution of gas usually continues for some hours, and, indeed, although it at length becomes very slow it appears never to cease altogether. At the end of the operation the stopcock on the reservoir is closed, and the gas contained in the apparatus is removed through the pump.

For the preparation of very small quantities of helium the mineral may be heated in a tube directly connected with the pump. For the quantitative determination of the yield of helium from a mineral the hard glass tube should be well packed with glass wool, to prevent traces of the powder from being carried away by the gas.

By the action of heat alone it would appear that only about one-half of the helium present in the mineral is given off, and in order to obtain the whole of the gas it is necessary to decompose the mineral by chemical processes. Heating with dilute sulphuric acid or fusion with acid potassium sulphate are the methods which yield the best results.

The second method requires the shortest time, but the decomposition of the mineral is never complete. The powdered mineral is heated in a hard glass tube or flask, attached to the apparatus already described, with an equal weight of acid potassium sulphate; the sulphate must be free from nitrate, and should be fused and powdered before it is used. The mixture froths considerably when it is heated, and consequently the flask or tube must never be more than half filled with it.

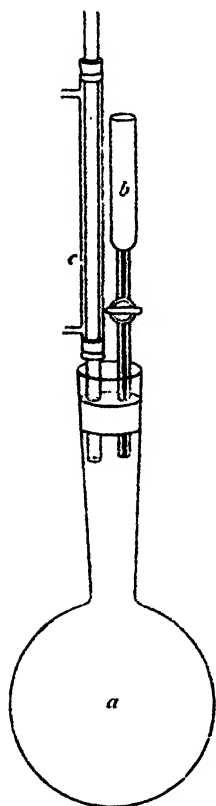


FIG. 74.

The decomposition of the mineral with dilute sulphuric acid (one in four of water) is more complete, but the time required is usually a week or even longer. The mineral is placed in a round-bottomed flask *a* (Fig. 74) with a tapered neck. A rubber stopper, which passes some way into the neck of the flask, has two holes bored in it for the passage of a short condenser and a tap-funnel. Mercury is poured into the space above the rubber stopper to render all the junctions air-tight. The apparatus communicates, through a tap at the top of the condenser, with the mercury-pump, which should be without a phosphorus pentoxide tube.

The apparatus is exhausted before the dilute acid, which should be previously boiled, is admitted; to facilitate the removal of the last traces of air, carbon dioxide may be admitted through

the tap-funnel and removed by exhaustion two or three times. The flask is heated on a water-bath, and the gas which is evolved may be removed by opening the tap communicating with the pump.

*Estimation of the total helium present in a mineral.*—The mineral is heated in a sealed tube with dilute sulphuric acid, and the gas is collected by the method described on p. 35. The complete decomposition of the mineral often requires some days at 150° C.

The discovery of helium and argon (p. 99) gave rise to the questions:—"Are these substances homogeneous?" and "Are they the only members of the group to which they belong?" Assuming that these gases are monatomic, as is indicated by their having the ratio 1.66 for their specific heats, their atomic weights are 4 and 40 respectively, and they occupy the positions indicated in the periodic table of the elements. This being the case, it appeared highly probable that there should exist a similar element X of atomic weight 20, and others Y and Z of higher atomic weight, occupying positions next to bromine and iodine. The search for these elements, and the working out of their physical properties, occupied five years, but it is now proved conclusively that there exists a series of five gaseous elements of which the atomic weights are in accordance with those predicted by the periodic law (*Phil. Trans.* 1901, vol. cxcvii. 47).

TABLE OF ATOMIC WEIGHTS

Hydrogen . . . . .	1	Helium . . . . .	3.96	Lithium . . . . .	7
Fluorine . . . . .	19	Neon . . . . .	20	Sodium . . . . .	23
Chlorine . . . . .	35.5	Argon . . . . .	40	Potassium . . . . .	39
Bromine . . . . .	80	Krypton . . . . .	82	Rubidium . . . . .	85.5
Iodine . . . . .	127	Xenon . . . . .	128	Cæsium . . . . .	133

Shortly after the discovery of helium, it was shown by Runge and Paschen that the lines of its spectrum could be divided into two sets, and that each set consisted of a primary and two subordinate series of lines of which the vibration frequencies could be expressed by a logarithmic formula. They attributed this to the presence of two substances in the gas, and from analogy with known cases they assigned the spectrum which was the more displaced towards the violet, to the lighter gas. The two



elements they named helium and parhelium: the spectrum of the first contained the line  $D_3$  ( $\lambda = 5876$ ), while that of the second contained the bright green line ( $\lambda = 5016$ ), which is next in brilliance to the yellow line. In proof of their theory they showed that when clévite gas was allowed to enter a vacuum tube through a porous plug, the glowing gas emitted a brilliant green light, and the green line was the strongest line in the spectrum. This they attributed to the separation of the lighter gas by diffusion.

Though the fact that the spectrum of helium contains two sets of lines, or rather that the two spectra of helium exist with almost equal brilliance under one set of conditions (their relative intensities being merely modified by change of pressure), remains unexplained, the conclusions drawn by Runge and Paschen have been shown to be fallacious. The change in the nature of the glow can be brought about by change of pressure alone (*Proc. Roy. Soc.*, 1897, **60**, 449), and indeed the tube of parhelium exhibited at the British Association meeting at Ipswich in 1897, contained the gas under so low a pressure that it phosphoresced (p. 311).

That helium does not consist of two constituents can be proved in the following manner. When the electric discharge is passed through the gas in a vacuum tube with platinum electrodes, the platinum volatilises and is deposited on the glass. The metal, which appears to be amorphous, absorbs the helium during its deposition, and the glow in the tube becomes green in colour. If this change were due to the removal of one of the constituents, the gas which is absorbed by the platinum, and which can be obtained by heating the tube with a Bunsen burner, should give the yellow spectrum only; but this is not the case. Further, it should be possible to obtain at least a partial separation of the constituents by the process of fractional diffusion, or by fractional solution in water, or in liquid oxygen. Experiments in this direction (p. 310) have led to the conclusion that the gas from clévite, or other minerals, contains only helium with a very small quantity of argon.

The search for the missing elements in the gases evolved on heating minerals, meteorites, etc., in those from natural waters and from mineral springs, was without success, and about the end of 1897 it appeared that all available sources were well-nigh exhausted.

There remained, however, the possibility that the missing element or elements might exist in atmospheric air—a constituent of the so-called argon, for, as Dr. Johnstone Stoney has pointed out, it is possible for a planet of the mass of the earth to retain on its surface gases of density 9, the density of water vapour. Some time previously we had discussed the possibility of separating the possible constituents of argon by the process of fractional distillation, and of determining the nature of the substance which, according to Olszewski, separated from helium when that gas was compressed and allowed to expand at the temperature of liquid air. As we had no means of obtaining liquid air we were at the time obliged to abandon the project.

About the time referred to, Dr. W. Hampson kindly offered to supply us with liquid air, and in February 1898 we commenced the preparation of a large quantity of argon (p. 105) for the purpose of the investigation. By the end of May, about 15 litres of the gas had been obtained, and on fractional distillation it yielded a quantity of a gas of density intermediate between that of helium and argon. This gas, to which we gave the name neon, was afterwards shown to contain a small quantity of helium (p. 217).

While these experiments were in progress, about the middle of May 1898 we obtained about a litre of liquid air for the preliminary experiment. The liquid was allowed to evaporate, and when only a few cubic centimetres remained, the gas was collected in a gasholder. After removing the oxygen and nitrogen, the residual inactive gas was examined spectroscopically; the spectrum was that of argon, but beyond this two brilliant lines, one yellow and one green, were observed.

This gas we at first supposed to consist of argon mixed with a heavier gas, to which we gave the name krypton. Subsequently, however, we found that there were two heavy gases present, and to the denser we gave the name xenon (p. 219).

The methods by which these gases were separated and purified are detailed elsewhere, and it is only necessary to state here that they all appear to be chemically inactive, though it is probable that under certain conditions of temperature and pressure helium would combine with one of the constituents of the minerals from which it is obtained, and in which it is probably present in a state of combination (*Proc. Roy. Soc.* **62**, 325; **64**,

130). It must be remembered that mercury, which somewhat resembles the rare gases with regard to its low boiling-point and monatomic character, would be chemically inactive at  $1000^{\circ}\text{C}$ .

A. M. Kellas (*Proc. Roy. Soc.* **59**, 66) and Th. Schloesing jr. (*C. r.* **121**, 605) have independently determined the quantity of argon (containing neon) in atmospheric nitrogen. In 100 c.c. of nitrogen Kellas found 1.186 c.c. of argon, which agrees with the number 1.183 given by Schloesing. This quantity of argon is just sufficient to account for the difference between the densities of atmospheric and chemical nitrogen.

It is difficult to form a very exact estimate of the quantities in which the individual gases are present in the atmosphere. From the quantities of the gases obtained by the distillation of atmospheric air, or of argon, the following numbers have been taken:—

Helium	1 to 2 parts per	1,000,000 of air
Neon	1 to 2 ..	100,000 ..
Argon	0.937 ..	100 ..
Krypton	1 ..	1,000,000 ..
Xenon	1 ..	20,000,000 ..

It is highly probable that the helium quickly passes out from our atmosphere into space—at least the speculations of Dr. Johnstone Stoney lead us to believe that this would be the case with a gas of so low a density. The quantity of helium, which is continually being given off by mineral springs, is, however, enormous, so that it is probable that the amount present in the atmosphere does not tend to diminish.

## CHAPTER XII

### THE DETERMINATION OF DENSITY

Choice of a standard—Direct and indirect methods—The density globe and counterpoise—Change of volume in density globes—Weighing—Densities of small quantities of gases, methods of manipulation, calculation of results—Sources of error—Density of water—Historical—Rayleigh's researches—Leduc's researches—Morley's researches—Review of results—Indirect determination of density, Schloesing's hydrostatic "method"—Avogadro's hypothesis.

THE density of any substance is usually defined as the ratio of the mass of it which fills unit volume to the mass of unit volume of some standard substance.

The densities of gases, like those of solid or liquid substances, are ultimately referred to the density of water (p. 127), or are expressed in terms of the standard units of mass and volume, the Paris kilogram and litre.

Since, however, the relative densities of gases approximate closely to half their relative molecular weights, it is convenient to express them, not only with regard to water, or in terms of grams per litre, but also with regard to some standard gas.

Since hydrogen is the lightest known gas, it would be convenient to take it as a standard, and to consider its density as unity. On the other hand, on account of the great difficulty in determining its density correctly, it has been found more convenient to take the density of oxygen as 16, and to calculate the densities of other gases on this basis.

In determining the mass of unit volume of a gas, or the relative densities of two gases, it is further necessary to take into consideration the conditions of temperature and pressure under which they are confined, and since all gases do not expand and contract equally with equal changes of temperature and pressure, the

densities should be expressed not only under definite conditions, but under standard conditions. Densities of gases are usually stated at the melting-point of pure ice, under a pressure equivalent to 760 mm. of mercury, at sea-level in the latitude of Paris. A correction for the value of the gravitation constant must be applied to results obtained in different parts of the globe, in order to render them directly comparable (p. 1).

The determination of density by the direct method consists in weighing the gas in a globe of known capacity under definite conditions of temperature and pressure. The globe in which the gas is weighed consists of a spherical glass bulb sealed to a capillary glass stopcock which should be very carefully worked. In order to eliminate errors due to changes in the atmospheric temperature and pressure, and consequently to change in the buoyancy of the globe, a closed bulb having the same external volume as the density globe is used as a counterpoise during the weighing. Further, since the weight of the globe varies somewhat with atmospheric conditions owing to the condensation of moisture on its surface, and since this condensation appears to depend upon the chemical composition of the glass, both the globe and counterpoise should be made of the same glass. This is particularly important in the case of small bulbs, where the surface of the glass is relatively large. As a matter of convenience, both the globe and counterpoise should be as nearly as possible of the same weight.

*Dimensions of the weighing globe.*—The accuracy of the result will, of course, in a great measure depend on the quantity of gas to be weighed, and consequently upon the volume of the weighing globe. With a good balance there should be no difficulty in weighing to 0.00005 gram., with a mass of 20 grams. on each pan, and it should therefore be possible to determine the density of air to within 0.2 per cent, or of helium to within 1 per cent accuracy, using a globe holding 30 c.c. A globe of 33 c.c. capacity was actually used in a large number of determinations of the density of helium and neon with satisfactory results; in weighing xenon a globe of 7 c.c. capacity was employed. A globe of 160 c.c. capacity was used in the case of argon, and for gases which could be obtained in quantity.

*Determination of the capacity of the globe.*—If the gas is to be introduced into the globe at the atmospheric temperature, its

capacity may be determined at about  $16^{\circ}$ ; the expansion of the glass may be neglected.

The globe should first be thoroughly cleaned and dried, and the stopcock lubricated, taking care that the hole in the plug is free from grease: it should then be exhausted and weighed. After weighing, the globe should be filled with boiled water, and suspended in a basin of water for an hour or more at constant temperature. After observing the temperature, and closing the stopcock, the water should be removed from the capillary tube above the tap, and the bulb carefully dried and suspended from the balance for the second weighing. The weights which are employed in the determination of the capacity of the globe must, of course, be reduced to the same standard as those which are used in weighing the gas. The results then express the density of the gas relatively to water (see also p. 227).

*Change in volume of density globes.*—It is well known that glass vessels continue to contract for some time after they are blown, and it appears probable that a considerable change may take place in the volume of a density globe, particularly if it is allowed to remain exhausted for a considerable time. A globe of capacity 33 c.c. was found to have suffered a considerable contraction between May and October in 1895. It had remained exhausted during the greater part of the summer, and when its volume was redetermined in 1898 a further decrease in volume was observed.

*The weights.*—Although the determination of the density of a gas really implies the determination of the weight of unit volume, it is quite unnecessary that the absolute values of the weight should be known, since the volume of the density globe is determined from the weight of water which it contains. It is, however, necessary that their relative values should be determined.

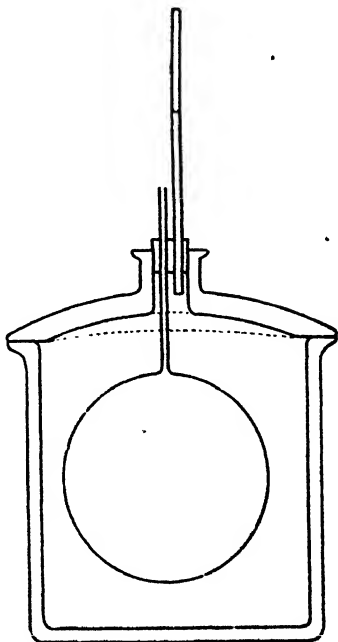


FIG. 75.

Lord Rayleigh (*Proc. Roy. Soc.* **53**, 362) has pointed out that a considerable error is incurred by neglecting to correct for the loss of buoyancy of the weighing globe due to contraction on exhaustion. The contraction of the globe is easily determined in the following manner:—The bulb is placed as in Fig. 75 in a desiccator with a ground glass lid, so that the neck passes through a rubber-cork fitting into the hole in the lid; a graduated glass tube also passes through the cork. The outer vessel is filled with water, and the position of the liquid in the graduated glass tube noted. The bulb is then exhausted, and the decrease in volume measured by determining the fall of the column of water in the tube. The vessel must be covered with powdered ice, or kept at constant temperature during the operation.

The following figures give an idea of the magnitude of this correction:—

	Volume of Ball.	Decrease of Volume.	Correction in Grams.
Ramsay .	162.782 c.c.	0.0212 c.c.	0.000027
Rayleigh .	1800 „	0.25 „	0.00056
Morley .	8793.9 „	1.41 „	0.00186
Morley .	21557.8 „	8.07 „	0.01041

The correction may be added directly to the observed weight of the gas contained in the globe.

Morley (p. 130) applied the correction by constructing two small globes, having the same weight *in vacuo*, whose volumes differed by the amount of the contraction of the weighing globe on exhaustion. These globes were suspended from the balance when the density globe was weighed empty.

The densities of the rare gases were determined by weighing them in globes of capacities 163 c.c., 33 c.c., and 7 c.c. respectively. The apparatus employed (Fig. 76) and the methods of manipulation are as follows.

The burette A, which is intended to receive the gas, is connected with the reservoir D, and with a side-tube B, which lies close to it. The upper-part of the burette is made of the same diameter as the side-tube, that is to say, about 7 mm., in order to eliminate the correction for capillarity. A glass scale is placed directly behind the instrument, which may be attached to it by means of wire and pieces of cork.

By means of the two-way stopcock *a* the burette may be placed in communication with the density bulb, which is attached by means of a piece of rubber tube (p. 19) to the tube *C*, and with the pump through the stopcock *c*. The tube *C* may contain pentoxide of phosphorus, but this is usually unnecessary, and if the quantity of gas to be weighed is small and it is necessary to economise space, it is sometimes dispensed with. In the latter case it is replaced by a small tube about 1.5 cm. long and 3 mm. in diameter, filled with silver foil, in order to prevent small globules of mercury from entering the density globe.

The density globe is carefully cleaned, attached to *c*, and exhausted by means of the mercury pump. In order to prevent dust from settling on the globe it is enclosed in a cardboard box with a lid through which the stem and tap project. Subsequently, when the gas is introduced, a thermometer is inserted into the box in order to determine the temperature. When the exhaustion is complete, the tap on the globe and the tap *b* are closed, and the globe is removed to the balance-case. After hanging for an hour in the balance-case it is weighed.

The globe is then re-attached to the apparatus, the tap *c* opened, and the space between the globe and the tap *a* exhausted. Since a small quantity of the gas remains in the hole drilled in the plug of the tap *a*, the tap *b* is closed, the reservoir *D* lowered, and the tap *a* is turned so as to place the burette in communication with the pump. It is usual to lower the reservoir so that the mercury in both tubes lies a few centimetres below the tap; the tap *d* can then be turned, and the reservoir placed in its clamp.

When the exhaustion is complete, the tap of the bulb is opened

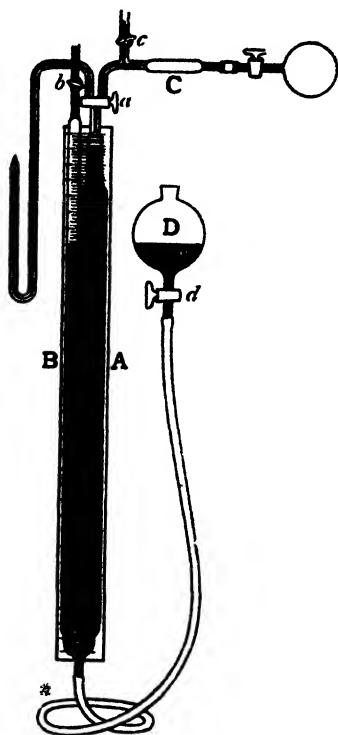


FIG. 76.



so as to make certain that no leakage has taken place. The tap *a* is then turned, the mercury allowed to fill the burette and side-tube, and the gas introduced into the burette through the syphon. The mercury drawn in after the gas is allowed to fill the syphon, but is not allowed to enter the capillary tube below the tap.

By closing the tap *c* and opening the tap *a* carefully the gas is allowed to enter the bulb. If the tube *c* contains pentoxide of phosphorus it is necessary to open the tap very slowly, or some of the powder may be carried over with the gas. If a large bulb is used it is necessary to fill the burette four or five times with gas. As the gas is usually stored in tubes this is not difficult. Sometimes only a small quantity of gas can be obtained, sometimes only 10 c.c. In this case the gas is allowed to flow into the bulb, the reservoir D being lowered till the mercury in the burette comes to rest at the top of the narrow portion. The mercury in the reservoir should not be at a lower level than the junction of the side-tube with the burette.

In measuring the pressure on the gas, the tap *b* is opened, and the mercury in the side-tube allowed to fall to the level of the mercury in the reservoir. In this operation it is usually necessary to close the tap *a* temporarily, for on account of the friction of the liquid in the rubber-tube the mercury in the burette may be forced up into *c*. If plenty of gas can be obtained, the mercury in the side-tube is brought to the level of the mercury in the narrow portion of the burette, gas being taken into or expelled from the burette through the syphon as may be found necessary. If the quantity of gas which can be obtained is insufficient to fill the globe at full pressure, the mercury in the burette is brought to the top of the narrow portion by raising the reservoir; the difference of level between the two surfaces is then read off on the mirror scale. Any final adjustment of pressures can be made by closing the tap *d*, and compressing the rubber-tube by means of a screw clamp.

The apparatus is usually allowed to stand at rest for half an hour before the final readings of temperature and pressure are taken. It is generally necessary to extinguish all gas-burners, and to keep the door of the room closed during the operation.

After taking the readings, the tap on the globe and the tap *a* are closed, and the reservoir raised to expel air from the side-

tube. The tap *b* is then closed, the reservoir lowered, and the tap *d* closed; the taps *a* and *c* are opened, and the whole of the gas which had not been introduced into the globe is removed by exhaustion. In this way it is possible to recover even the gas contained in the hole in the tap. The taps *a* and *c* are then closed, and the globe is removed to the balance-case, where it is allowed to remain for an hour before it is weighed.

After weighing the globe, it is again attached to the apparatus, and after removing the air from the space C, the gas is pumped out and collected. The globe can now, if necessary, be weighed again.

The weight of one litre of the gas can be calculated from the formula—

$$W = w \times \frac{(273 + t)}{273} \times \frac{760}{P} \times 1000,$$

where *w* is the weight of the gas contained in the globe of volume *v* at temperature *t*°, and under a pressure of *P* millimetres of mercury at 0° C., and *P* is the barometric pressure less the difference of the levels of the mercury in the manometer.

Since  $\frac{760 \times 1000}{v \times 273}$  is a constant and it may be denoted by *K*,

$$W = w \frac{(273 + t)}{P} \times K.$$

If the density of oxygen be taken as 16, and the weight of one litre 1.4295 grams.,

$$\begin{aligned} D &= w \frac{(273 + t)}{P} \times K \times \frac{16}{1.4295}, \\ &= w \frac{(273 + t)}{P} \times k, \end{aligned}$$

since the second factor is also a constant.

TABLE OF RESULTS

<i>Density of gas from Chloride -</i>				
Volume of globe.	Temperature.	Pressure.	Weight of gas	Density.
33.023	18.33	615.8	0.00190	2.187
33.023	17.10	763.2	0.00600	2.152
33.023	19.13	763.2	0.00610	2.205
				Mean 2.181
<i>Density of Argon—</i>				
160.17	13.34	742.8	0.26591	19.952
160.17	12.95	741.3	0.26586	19.961
32.762	16.15	758.1	0.05501	19.95
32.762	17.10	768.2	0.05550	19.98
32.762	16.65	764.3	0.05519	19.94
<i>Density of Neon—</i>				
7.152	18.30	422.5	0.00331	9.94
7.152	20.15	417.2	0.00320	9.80
The gas was sparked with oxygen between the two experiments.				
<i>Density of Neon—</i>				
7.152	21.60	245.4	0.01224	61.01
7.152	22.45	225.3	0.01076	63.74

The chief sources of error in the determination of density with small quantities of gas are due to the changes of surface condition of the glass. In order to eliminate such errors as far as possible, the globes should never be touched with the fingers, and should always be treated in exactly the same manner before each weighing. It is particularly important that the globes should never come in contact with mercury, as it is quite impossible to wipe small globules of mercury off the surface of the glass, and a very small trace would be quite sufficient to render the results valueless. Particular attention should be paid to the lubrication of the stopcock: every trace of grease should be carefully removed from the outside before the globe is weighed.

When the gas to be weighed can be obtained in large quantity, to avoid the trouble of pumping out the pentoxide of phosphorus tube, a density bulb with a two-way stopcock may be used (Fig. 77). The gas can then be allowed to flow away through

the second passage in the tap until the connecting tubes of the apparatus are free from air.

*The density of gases in a mixture.*—The determination of the density of gases may be applied to the analysis of mixtures containing two gases of known density. In the case of mixtures of helium and argon, for instance, the method was formerly the only one with which we were acquainted. Within the limits of accuracy of the methods for the determination of density which have been so far described, we may assume the law of mixture to hold good for the more perfect gases (see p. 139). If, then,

a mixture contains, in 100 volumes,  $n$  volumes of a gas of density  $d_1$ , and  $(100 - n)$  volumes of a gas of density  $d_2$ ,

$$d_1 n + d_2 (100 - n) = D \ 100.$$

It must not be forgotten that the accuracy of the result is not of a high order unless the coefficients in the equation are very accurately determined, and that in the case of gases such as sulphur dioxide, the deviations from the simple gas laws are considerable.

*Historical.*—Although the early attempts to determine the density of gases by John Dalton, Berzelius, Biot and Arago, Dumas and Boussingault, and others, are of interest historically, it would serve no purpose to give an account of their researches here.

The first accurate work in this direction was carried out by Regnault about the year 1845. The introduction of the counterpoise globe rendered it possible to eliminate errors due to the change of buoyancy of the air, owing to changes of temperature and pressure during the experiment, and enabled him to obtain results which bear comparison with those of modern investigators. The results as expressed by him show, however, a constant difference from what appear to be the true values for the densities of the gases which he examined. He had not observed that the globe in which the gas was weighed decreased in volume when exhausted. As was subsequently pointed out by Rayleigh, this change in volume involves a correction for loss of buoyancy. Regnault's results were corrected by Crafts (*C. r.* 106,

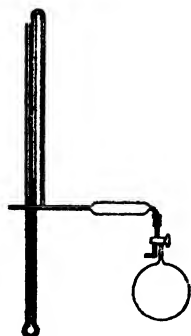


FIG. 77.

1662) in 1888. Since Regnault's density globe had been broken, another of the same dimensions (10 litres capacity) and of the same weight was obtained. The correction amounted to 3 milligrams, which was added to the result of each weighing.

Within the last few years the densities of the principal gases have been accurately determined by Ledue, by Lord Rayleigh, and by Morley. Of these investigations, Lord Rayleigh's are of par-

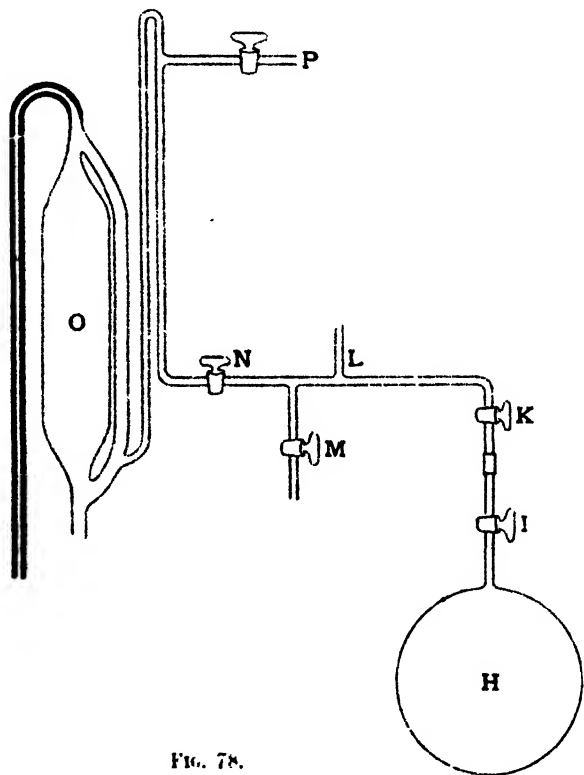


FIG. 78.

ticular interest, both with regard to the simplicity of the methods employed, and to the accuracy of the results, so far as can be judged from the concordance of individual results obtained by weighing samples of gas from different sources.

The gases were weighed in a globe of known volume, into which they were introduced at the temperature of melting ice, and under a definite pressure independent of the atmospheric pressure. By exhausting the upper chamber of the manometer (Fig. 79) and the weighing-globe by the same pump, the error

due to the pressure of air in the latter when exhausted was eliminated. The globe, which was balanced against a counterpoise, had a capacity of 1800 c.c., and weighed 200 grams. when empty. The correction for loss of buoyancy on exhaustion amounted to 0.00056 gram. Its volume was determined by filling it with water at  $0^{\circ}$  C. and weighing it; the density of the water was taken to be 0.99988. In order to avoid the difficulty introduced through the expansion of the water, the weighing was carried out in frosty weather.

The gas was introduced into the globe by means of the apparatus shown in Fig. 78. The globe H, which is placed in a vessel containing powdered ice, is connected through the tap I to the apparatus. The taps M and N lead to the vessel in which the gas is generated, and to the Töpler mercury-pump O. The apparatus is also connected through P and L to the upper and lower reservoirs of the mercury manometer shown in Fig. 79.

After thorough exhaustion a small quantity of gas was introduced into the globe and removed through the pump; the globe was then filled with it at normal pressure. The final adjustment was made by bringing the mercury to the level of the two points AA' in the manometer.

The manometer which served for the measurement of pressure was constructed so as to eliminate errors due to the inequalities of the glass, etc. An iron rod carrying two points AA' passed through rubber junctions H and F into the reservoirs B and C. The rubber tubes were covered by mercury contained in the cups K and G. The two reservoirs were connected by a tube E, so that when the lower one contained mercury and the upper one was exhausted the mercury rose to the level of the point A. In adjusting the pressure in the globe, the mercury was maintained at the level of the point A by allowing mercury to enter or leave the lower reservoir through the tube R. At the

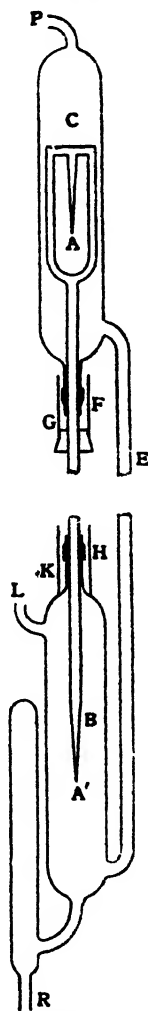


FIG. 79.

same time the tap M was opened or closed so as to alter the pressure of the air in the globe, and so bring the mercury to the

\* level of the upper point. The distance between the two points was measured before the apparatus was set up, and it was only necessary to apply a temperature correction to obtain the pressure on the gas in the globe.

The following figures were obtained for the weights of different gases contained in the bulb under a pressure of 762.511 mm. of mercury at 14.85° C., the globe being immersed in melting ice.

#### *Oxygen—*

Prepared by electrolysis, 2 experiments	2.6272 + 0.00056 gm.
„ „ 1 experiment	= 2.6271 + 0.00056 „
„ from potassium chlorate, 5 experiments	= 2.6269 + 0.00056 „
„ „ „ 5 „	= 2.6269 + 0.00056 „
„ „ „ permanganate, 1 experiment	= 2.6271 + 0.00056 „
Mean result, 2.62760.	

#### *Nitrogen (atmospheric)*

From air, by hot copper	2.3103 + 0.00056 gm.
„ by hot iron	= 2.3100 + 0.00056 „
„ by ferrous hydrate	= 2.3102 + 0.00056 „
Mean result, 2.3107.	

#### *Nitrogen—*

From ammonium chloride and sodium nitrite,	
3 experiments	= 2.2987 + 0.00056 gm.
„ urea, 4 experiments	= 2.2985 + 0.00056 „
nitrous oxide	= 2.2990 + 0.00056 „
nitric oxide	= 2.3001 + 0.00056 „
Mean result, 2.2994.	

#### *Air free from water and carbon dioxide—*

	Weight of gas contained in the globe.
Highest of seven results	2.37686 + 0.00056
Lowest „ „	2.37647 + 0.00056
Mean „ „	2.37661 + 0.00056

In order to compare these results directly with those obtained by other observers, it was necessary to express them in terms of the weight of one litre, at the pressure equivalent to 760 mm. of mercury at Paris.

To correct for pressure, the observed weights were multiplied by the factor 0.99974. But since the measurements were made in latitude 51° 47', it was necessary to introduce a correction for

gravity. This was easily effected by multiplying by the factor  $\frac{980.939}{981.193}$ , the ratio of the gravity constants at Paris and in latitude  $51^{\circ} 47'$ .

The mean corrected values now become :—

Air.	Oxygen.	Nitrogen.
2.37512	2.62534	2.30883

The weights of one litre :—

Air.	Oxygen.	Nitrogen.
1.29327	1.42952	1.25718

Lord Rayleigh has also determined the densities of other gases by means of the same apparatus. The results obtained for the density of carbon monoxide will indicate the degree of accuracy with which the experiments were performed. Three sets of experiments were made in which the gas was obtained from entirely different sources. The figures represent the weight of gas contained in the globe; the weight of the same volume of oxygen under similar conditions being  $2.62704 + 0.00056$  gram.

Method of preparation (see p. 49).	Weight of gas.
From potassium ferrocyanide and strong sulphuric acid	$2.29843 + 0.00056$
From oxalic acid and strong sulphuric acid	$2.29852 + 0.00056$
From sodium formate and 70 per cent sulphuric acid	$2.29854 + 0.00056$

Leduc has determined the densities of the commoner gases by weighing them, under known conditions of temperature and pressure, in glass globes of about 2.3 litres capacity. The weak point in the method which he employed lies in the fact that the globes were never completely exhausted. A pump was used which would exhaust down to a pressure of about 0.1 mm.: that is to say, that about  $\frac{1}{800}$  part of the gas would remain in the globe. A pressure of this order would be quite impossible to measure directly, and might vary between 0.05 mm. and 0.15 mm.; the error introduced in this way is of the same order of magnitude as the difference between the weights obtained by Lord Rayleigh and Leduc for a litre of air—

	Leduc.	Lord Rayleigh.	$\Delta$
Weight of one litre of air	1.29316	1.29327	0.00011
			or $\frac{1}{11786}$



Leduc's results are consistently lower than those of other observers, except in the case of nitrous oxide; the discrepancies may, perhaps, be accounted for in this way:

In a *résumé* of his researches on the densities of gases, Leduc states that the agreement between the values which he obtained for the densities of oxygen, nitrogen, and atmospheric argon, are in accordance with his own determination of the composition of air (p. 97), the determinations of the quantity of argon in air by M. Schloesing and Dr. Kellas, and the density of argon by Lord Rayleigh and Prof. Ramsay. The statement contains certainly one fallacy, in that he assumes that the number 19.94 represents the density of argon with regard to that of hydrogen as unity, and not to oxygen as 16, and further, it is probable that the air contains more nearly 19.9 than 20.0 per cent of oxygen.

A very elaborate investigation of the densities of oxygen and hydrogen has been carried out by Dr. Morley, and described in the *Proceedings of the Smithsonian Association*. The methods employed are of too complicated a nature to be dealt with in detail, but as the work is of the greatest importance, it may be as well to describe it briefly.

The experiments were performed in such a manner as to eliminate all known sources of error. Special attention was paid to measurements relating to temperature and pressure, and the volume expansions of each of the gases were considered independently. The globes were of capacities varying from 8 to 20 litres; their capacities were accurately determined by an indirect method involving weighing them in water; and their contraction on exhaustion was estimated and corrected for in the manner described on p. 120.

The weights of the gases were determined by suspending the globes alternately from the right and left pans of the balance, after the method of Gauss. The results are reduced to the values which would have been obtained at sea-level in latitude 45°. They may be reduced to the Paris standard by multiplying by 1.000316.

*Density of oxygen* (Preparation of oxygen, see p. 43).—Three series of experiments were made under different conditions—

1. The bulbs were filled with oxygen at temperatures, determined by means of mercurial and air thermometers, varying

between  $15^{\circ}$  and  $20^{\circ}$ . The apparatus was connected with an open manometer, standing in the same trough with a barometer. The readings were taken with reference to a glass scale placed in front of the tubes, which were 19 mm. in diameter, by means of a cathetometer.\* The difference between the readings of the two instruments gave the pressure under which the gas was confined. The results had afterwards to be corrected by addition of  $300\frac{1}{100}$ , on account of an error which was found to exist in the standard of length; the mean results alone are corrected.

2. The globe was immersed in powdered ice and connected with one limb of a differential manometer, which was also connected with a vessel filled with pure hydrogen immersed in ice. The mercury in the manometer was brought into position with regard to two projecting points in the opposite limbs; the pressure required to bring the mercury to this position had previously been determined.

In this series of experiments the globes were kept in a desiccator, from which the stopcocks and leading tubes alone projected. The various operations involved in exhausting, filling, and weighing them were performed mechanically.

3. The globes were immersed in powdered ice, and the pressure was determined directly, by connecting the interior of the apparatus with the lower chamber of a barometer.

TABLE OF RESULTS

		Weight of one litre.	Difference.	Volume of Bulb.
SERIES I 9 experiments	Highest	1.42907	0.00049	{ 21.5693 litres 8.8367 "
	Lowest	1.42838		
Mean 1.42879 $\pm$ 0.000034				
SERIES II 6 experiments	Highest	1.42880	0.00029	{ 20.0576 .. " "
	Lowest	1.42851		
SERIES II (b) 9 experiments	Highest	1.42896	0.00043	{ 20.5578 .. " "
	Lowest	1.42853		
Mean (15) 1.42887 $\pm$ 0.000048				
SERIES III	Highest	1.42957	0.00047	{ 8.000 .. " "
	Lowest	1.42910		
SERIES III (b)	Highest	1.42951	0.00102	{ 15 0 .. " "
	Lowest	1.42849		
Mean 1.42917 $\pm$ 0.000048				

In calculating the final mean the third series is given double weight.

Weight of one litre of oxygen =  $1.42900 \pm 0.000034$ .

*Hydrogen.*—Five series of experiments were made, but the two first sets were subsequently neglected, as the results appeared to be affected by a constant error, the nature of which could not be determined.

In Series I and II the globes were directly weighed after filling with hydrogen, but in the three last series an entirely different plan was adopted. Three of the globes were connected together by means of glass tubes, and immersed in a large cylinder filled with powdered ice: precautions were taken to prevent the pressure of the ice from altering the size of the globes. The capacities of the globes were already known, the volume of the leading tubes, which were also connected with the lower reservoir of a barometer, was also determined. Palladium foil, contained in a glass tube, was charged with pure hydrogen: the palladium was capable of absorbing between 3 and 4 grams of the gas. The tube was then sealed, weighed, connected with the tube leading to the globes, and heated. The volume of the gas given off was estimated from the barometer readings, its weight was determined by detaching the palladium tube, and reweighing it. The details of the operations involved are carefully described in the original memoir (*loc. cit.*). The following is a general summary of the results:—

Series I . . . . . Mean 0.089938  
 „ II . . . . . „ 0.089970 } These results were rejected.

The results of the last three series all appear to be of equal weight—

Series.	Highest.	Lowest.	Mean.	Experiments.
III	0.089912	0.089856	0.089886	8
IV	0.089972	0.089777	0.089880	6
V	0.089877	0.089830	0.089866	..
Final mean 0.089873 $\pm$ 0.000027				

In the following table the results obtained by different observers are stated:—

DENSITIES OF THE COMMONER GASES EXPRESSED IN TERMS  
OF GRAMS PER LITRE

	Air.	Oxygen.	Nitrogen.	Hydrogen.
Regnault . . . . .	1.29319	1.42980	1.25617	0.08958
Corr. by Crafts . . . . .	1.29349	1.43011	1.25647	0.08988
Von Jolly . . . . .	1.29351	1.42939	1.25787	...
Corr. . . . .	1.29383	1.42971	1.25819	...
Leduc, 1891 . . . . .	1.29316	1.42910	1.25709	0.08985
Rayleigh, 1893 . . . . .	1.29327	1.42952	1.25718	0.09001
Morley . . . . .		1.42900		0.089873
.. (Paris standard) . . . . .		1.42945		0.089951

The true values for the densities of oxygen, nitrogen, and air probably lie between the values given by Rayleigh and Leduc respectively. It is probable that Morley's determination of the density of hydrogen is the most correct. Lord Rayleigh's value for it is certainly slightly too high.

*Indirect method for the determination of the density of a gas.*—Schlösing (*C. r.* **126**, 1898, 220 and 476) has devised a hydrostatic method for the determination of the density of moderately heavy gases when only very small quantities can be obtained. The apparatus employed is shown in Fig. 80. The tubes A and B, which are from 1000 to 1600 cm. in length, and have an internal diameter of about 2 or 2.5 mm., are enclosed in a water jacket. At the bottom they are sealed to a three-way tap, so arranged that either of them can be connected with the other, or with a mercury reservoir. Both tubes are open at their upper ends.

The tubes are first completely filled with mercury, and the gas G, of which it is required to determine the density, is admitted so as to fill one of them; the other tube is filled with carbon dioxide, or some gas which is heavier than G, and which has no chemical action upon it. When the stopcock is turned so as to place the tubes in communication, the carbon dioxide, in virtue of its superior density, will sink in the tube;

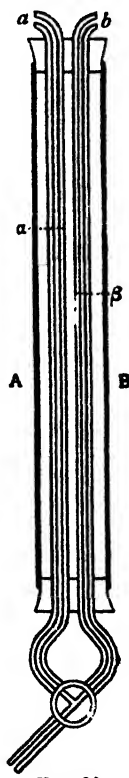


FIG. 80.

at the same time some of the gas G will be expelled, and air will enter on top of the carbon dioxide as its level falls. From six to eight minutes must elapse before equilibrium is established.

If the tube A had previously contained carbon dioxide, and the tube B the gas, G, which was heavier than air, and  $\alpha$  and  $\beta$  are the surfaces of contact of these gases with carbon dioxide, the condition of equilibrium will be represented by the equation,

$$h'd' = hd + h' - h'\delta.$$

Where  $h$  and  $h'$  are the distances from the centres of the orifices  $\alpha$  and  $b$ , to the points  $\alpha$  and  $\beta$ , and  $d$ ,  $d'$ , and  $\delta$  are the densities of air, the gas G, and carbon dioxide under similar conditions of temperature and pressure. The correction for the pressure of water-vapour is eliminated by saturating the gases before they are brought into the apparatus.

To determine the positions of the points  $\alpha$  and  $\beta$ , the small gas pipettes, are attached to the open ends,  $a$  and  $b$ , of the tubes, and the carbon dioxide is absorbed. When the gas is returned to the tube the mercury will occupy, in each case, the space formerly occupied by the carbon dioxide.

	Time allowed for taking Readings.						Calculated Density of Air = 1.
	2.	4.	6.	8.	10.	12.	
Air.	...	1.000	0.999	0.998	...	...	1.000
Nitrogen	0.990	0.968	0.967	0.967	0.966	0.966	0.967
Oxygen	1.176	1.107	1.105	1.105	1.104	1.104	1.105
Methane	...	...	0.559	...	0.557	...	0.558

With hydrogen the results were not satisfactory. This is probably due to the escape of gas by diffusion, from the upper part of the tube.

*Deduction of the density from the ratio of the specific heats.*—

The density of a gas may also be determined from the velocity of sound in it, if the ratio of its specific heats at constant pressure and constant volume is known (p. 271).

*Avogadro's hypothesis.*—Since the simple laws which govern the relationship between volume, temperature, and pressure in gases are only accurate within certain limits, it might be

expected that Avogadro's hypothesis would also be only an approximation. By comparing directly the densities of gases and their molecular weights as determined by chemical means, it will be at once seen that the ratios do not give a constant value, and that consequently the space occupied by a molecule must vary slightly among the different gases.

Gas.	Density, 0. 16.	Molecular Weight, $\times 0.5$ . (Calculated from the chemical equivalent.)	
Hydrogen . . . . .	1.006	1.00	1.0076
Nitrogen . . . . .	14.071	13.93	14.04
Oxygen . . . . .	16.000	15.88	16.00

Numerous investigations have been undertaken with a view to determining the exact proportion in which oxygen and hydrogen enter into combination to form water. Berzelius and Dulong (*A. de Ch. et de Ph.* [2], 15, 389) determined the ratio by reducing heated copper oxide with pure hydrogen, and determining the quantity of water formed. They obtained as a mean result for the atomic weight of oxygen the number 15.894. By the same method Dumas (*A. de Ch. et de Ph.* [3], 8, 200) obtained the value 15.961, and Erdmann and Marchand (*J. für pract. Ch.* 26, 468) the number 15.975.

These results are now interesting only from an historical standpoint; the ratios, as determined by a number of more recent investigations, appear to show that the atomic weight of oxygen is less than 15.9.

The following is a list of the more important investigations—

		Substances weighed.	Atomic Weight of Oxygen (H = 1).
Cooke and Richards . . . . .	<i>Am. Ch. J.</i> 10, 81, 191 . . . . .	H and O	15.869
Keiser . . . . .	<i>Am. Ch. J.</i> 10, 249 . . . . .	H and H <sub>2</sub> O	15.950
" . . . . .	<i>Am. Ch. J.</i> 20, 735 . . . . .	H and H <sub>2</sub> O	15.869
Noyes . . . . .	<i>Am. Ch. J.</i> 1890, 12, 441 . . . . .	H and O	15.877
Dittmar and Henderson . . . . .	<i>Phil. Soc. of Glasgow</i> , 1891 . . . . .	O and H <sub>2</sub> O	15.866
Rayleigh . . . . .	<i>Proc. Roy. Soc.</i> , 1889, 45, 425 . . . . .	H and O	15.89
Leduc . . . . .	<i>Comptes rendus</i> , 115, 43 . . . . .	O and H <sub>2</sub> O	15.881
Morley . . . . .	<i>Smithsonian</i> , 1895 . . . . .	H and H <sub>2</sub> O	15.879
" . . . . .	" . . . . .	O and H <sub>2</sub> O	15.879

To this we have to add the atomic weight calculated from the volume relations and densities of the gases.

Scott . . . . .	15.868
Morley . . . . .	15.879

Cook and Richards, Noyes, and Leduc, all employed methods similar to that of Berzelius. The former compressed hydrogen into an exhausted glass globe, and burned the gas in contact with heated copper oxide. This method avoids the difficulty of determining the weight of the hydrogen, a small weight at the best, by difference only. Leduc, who performed two experiments only, reduced a weighed quantity of copper oxide, and weighed the water formed. The hydrogen absorbed by the copper was estimated by reoxidation.

The first experiments of Keiser are certainly inaccurate, but the use of palladium in order to absorb and weigh the hydrogen introduced a new feature. This method in the hands of Morley gave, at a later date, the most accurate results which have yet been obtained.

Rayleigh's method consisted in weighing the gases in glass globes and transferring them to an apparatus in which they were mixed and burned. The globes were subsequently reweighed, and the residual gas was analysed. If Morley's density for hydrogen be substituted for Rayleigh's, the number becomes more nearly 15.87.

Scott (*Phil. Trans.* 1893) determined directly the volume of oxygen and hydrogen which enters into combination to form water. The gases were measured in a constant volume burette; the mercury in each experiment was brought to a mark on a portion of the vessel which was made very narrow. The mixture was exploded in successive quantities. The excess of gas unconsumed was measured and analysed.

In the earlier experiments the tap of the explosion pipette was lubricated with a hydrocarbon grease. This led to the formation of a layer of grease on the inside of the pipette, which was partially burnt during the explosion of the gases, with the result that the apparent quantity of oxygen consumed by the hydrogen was too large.

The results of the experiments are fairly concordant; the most probable result for the ratio of the volumes of oxygen to hydrogen is 1 to 2.00245.

Morley (*Smithsonian Contributions*, 1895) has determined directly the composition of water by burning weighed quantities of oxygen and hydrogen in a closed apparatus, and determining the weight of water produced, and the excess of gas remaining in the apparatus.

The combustion apparatus (Fig. 81) consisted of a glass cylinder, through the sides of which passed tubes which were ultimately connected with the apparatus delivering the oxygen and hydrogen respectively. The tubes terminated in small platinum jets which projected upwards into the cylinder; a pair of platinum wires placed immediately above them served for the ignition of the flame of oxygen or hydrogen. Externally the tubes were sealed to two tubes containing pentoxide of phosphorus, which formed part of the apparatus, and which served to prevent loss of water through diffusion, or during the final exhaustion of the apparatus. The apparatus was weighed against a counterpoise.

The oxygen was obtained by heating potassium chlorate, and was weighed in two of the density globes which were afterwards simultaneously connected with the combustion apparatus. The hydrogen was absorbed by metallic palladium, and weighed on an apparatus similar to that employed in the determination of the density of that gas. Forty-two litres of hydrogen and twenty-one litres of oxygen were employed in each experiment: the quantity of gas remaining uncombined varied from one six-hundredth to one ten-thousandth of the whole.

During the experiment the combustion tube was kept cool, so that the gases were drawn into it in a steady stream. It was possible to continue the combustion till the pressure of the water vapour and gas in the apparatus did not exceed 80 mm. of mercury. At the end of the experiment the oxygen globes and palladium tubes were closed and subsequently weighed. The gas

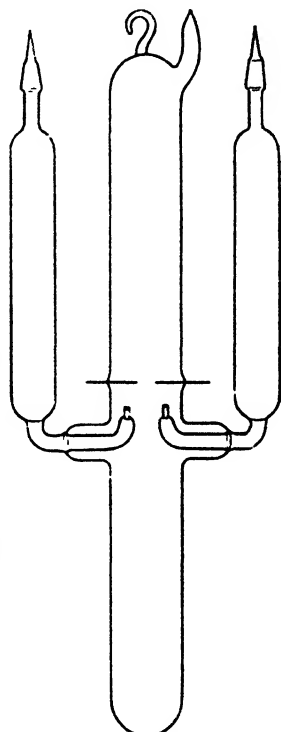


FIG. 81.



contained in the apparatus was removed by exhaustion and analysed, and the combustion chamber sealed and weighed.

*Sources of error.*—The gas contained in the apparatus was found to contain traces of carbon dioxide, and in some cases nitrogen. These impurities were traced to the asbestos used in the construction of the apparatus, and to the air remaining in the globes after exhaustion; the error introduced was inconsiderable. Experiments were conducted to determine whether the gases were completely dried by passage over pentoxide of phosphorus, or whether that substance absorbed an appreciable quantity of oxygen.

On the other hand it remained possible that traces of ozone or of hydrogen peroxide were formed during the combustion: if this were so the apparent quantity of oxygen consumed would be too great.

#### SET OF ELEVEN DETERMINATIONS

	Atomic weight of oxygen (H = 1).	Ratio $H_2O$ H.
Highest	15.882	17.883
Lowest	15.887	17.873

#### MEAN VALUE OF THE ATOMIC WEIGHT OF OXYGEN

From ratio O H	15.8792
From ratio $H_2O$ H	15.8785

Morley (*loc. cit.*) has also determined the composition of electrolytic gas in a manner similar to that employed for the determination of the density of hydrogen. A voltameter was constructed so that it could be weighed, and then connected with a system of globes of known capacity immersed in ice and water, and previously exhausted. The current was passed through the voltameter till the pressure in the apparatus became nearly normal; the pressure was then accurately determined, and the voltameter was detached and weighed again. The density of the gas was deduced from the volume (43 litres), temperature, and pressure of the gas and the loss of weight of the voltameter.

In each experiment the gas was analysed, and it was found that in every case excess of hydrogen was present. It would appear that during the process of electrolysis of the caustic soda solution contained in the voltameter, a certain quantity of the

oxygen entered into combination with other substances present. Whether hydrogen peroxide or ozone were formed or not was not determined.

•

WEIGHT OF ONE LITRE OF ELECTROLYTIC GAS

Highest . . . . .	0.535584
Lowest . . . . .	0.535441
Mean . . . . .	0.535510

Calculated directly from the density of electrolytic gas and the densities of hydrogen and oxygen, the ratio of oxygen and hydrogen in water becomes 1 to 2.0045.

It is necessary to take into account the fact that the law of mixture is only approximate. Applying Van der Waal's formula for the relations of temperature, pressure, and volume of gases (p. 176), and using the values of the constants deduced by Sarrau from Amagat's observations (p. 165), the ratio of the mixture becomes 1 : 2.00357. Applying a final correction for the slight excess of hydrogen (see p. 138) present in the gas, the final value 1 : 2.00269 was obtained. As to whether the correction for pressure is valid or not is a question; the results obtained for the compressibility of hydrogen are, as will be pointed out, open to criticism.

Keiser (*Am. Ch. J.*, 1898, 20, 72) has recently determined gravimetrically the proportions in which the gases combine. The hydrogen obtained by electrolysis of dilute sulphuric acid was absorbed by spongy palladium in a tube which also contained some pentoxide of phosphorus. The tube was weighed, and oxygen was admitted slowly till the whole of the hydrogen was consumed. The tube was then allowed to stand overnight; the excess of oxygen was removed by exhaustion, and the tube was weighed.

After standing for forty-eight hours the palladium was removed, and the tube was weighed again.

Typical experimental results:—

Weight of hydrogen.	Weight of oxygen + hydrogen.
0.27549.	2.45798

TABLE OF RESULTS

	Ratio H O	Ratio H, H <sub>2</sub> O
1 . . .	7.923 . . .	8.929
2 . . .	7.943 . . .	8.946
3 . . .	7.940 . . .	8.956
4 . . .	7.945 . . .	8.950
Mean . . .	7.937 . . .	8.943

Atomic weight of oxygen from ratio H O . . . . . 15.874

" " " " H H<sub>2</sub>O . . . . . 15.886

In 1898 Daniel Berthelot pointed out that the true molecular weight of a gas could be calculated from its density and the observed deviation from Boyle's law (*C. c.* 1898).

Where  $v_0$  is the volume occupied by a gram-molecule of the gas under pressure  $p_0$ , the deviation from the simple law may be expressed by

$$\frac{pv}{p_0v_0} = 1 + a'p - ap_0,$$

where  $v$  is the volume occupied by the gas under a very low pressure  $p$ .

If two gases have the same molecular volume under a very low pressure (p. 159):

$$v_0 = v_0^p \left[ 1 + a'p - ap_0 \right] = v_0^p \left[ 1 + a'p - a'p_0 \right]$$

$$v_0' = v_0^p \left[ 1 + a'p - ap_0 \right] = v_0^p \left[ 1 + a'p - a'p_0 \right]$$

If  $p$  is very small and  $p_0$  is one atmosphere,

$$\frac{v_0}{v_0'} = \frac{1 - a}{1 - a'}$$

If  $d, d', d''$ , etc., are the relative densities of different gases under atmospheric pressure, their relative molecular weight will be  $(1 - a)d, (1 - a')d',$  etc.

	Hydrogen.	Nitrogen.	Carbon monoxide.	Oxygen.
$a$ . . . . .	-0.000450	0.00038	+0.00046	+0.00076
$(1 - a)$ . . . . .	1.00046	0.99962	0.99954	0.99924
$d$ . . . . .	0.062865	0.87508	0.87495	1
Mol. wt. . . . .	2.01472	28.0132	28.0068	32
At. wt. . . . .	1.0074	14.007	C. = 12.007	16
At. wt. from results of analysis . . . . .	1.01	14.04	12.00	16

## CHAPTER XIII

### THE RELATIONSHIP OF TEMPERATURE, PRESSURE, AND VOLUME OVER LIMITED RANGES OF PRESSURE

Manometers and barometers—Temperature correction for height of column of mercury -- Gay-Lussac, Charles, Dalton, Rudberg, and Regnault—Pressure coefficients of expansion -- Experimental determination of the pressure coefficient -- The gas thermometer—Temperature on the absolute scale—Abnormal expansion -- The relations of temperature pressure and volume in rarefied gases -- The McLeod gauge.

THE simplest form of pressure gauge for the measurement of pressures lower than atmospheric pressure, consists of a piece of glass tube of uniform bore bent on itself (Fig. 82, *a*). The lower end of the longer limb of the tube is open, and dips below the surface of the mercury in a basin; the other end is connected to the apparatus to be exhausted. The height of the column of mercury in the tube is measured by means of a scale with an ivory point which is brought on to the surface of the mercury at each reading; or a barometer is placed in the basin by the side of the gauge, and the differences of level of the mercury in the two tubes is determined by means of a scale placed behind them.

A more convenient form of the instrument, which may be used for measuring pressures between 1000 and 10 millimetres, is shown in the next figure. The difference of level of the mercury in the U-tube is read off directly on a scale placed behind it. Sometimes, if the instrument is intended for the determination of reduced pressure only, the vertical tube is bent so as to bring the two surfaces of the mercury directly one over the other. Care must be taken to obtain a piece of tube of uniform bore, and this is not easy; the diameter of the tube should not be less than 7 millimetres.

For the measurement of pressures below 1000 millimetres it

is sometimes convenient to employ a closed vacuum gauge (Fig. 82, *c*). The upper end of one limb of the U-tube is sealed, and a trap is inserted to prevent traces of air from entering. The apparatus may easily be filled with mercury in the following manner.

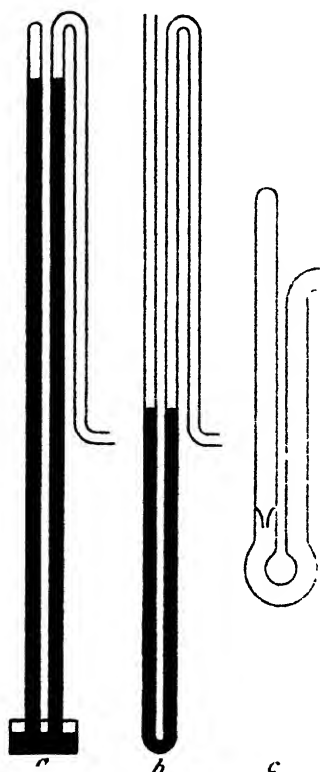


FIG. 82.

A glass bulb is sealed to the open limb of the manometer, and the whole apparatus is thoroughly cleaned and dried. Mercury is then introduced into the bulb, and the apparatus is connected with the water pump by means of a long rubber tube. By withdrawing and then readmitting the air, mercury from the bulb is allowed to run in small quantities into the closed limb of the U-tube. Each time mercury is admitted, the tube is carefully heated by means of a Bunsen burner, so that the mercury boiling in vacuo expels the whole of the air. The heating need not be continued after the tube is filled to above the level of the trap.

A *differential manometer* of great delicacy was employed by Morley (p. 131) in the determination of the density of oxygen. Two bulbs connected by a U-tube contained glass points projecting downwards. The mercury, which half-filled each bulb, was brought to the level of the glass points in each experiment. The whole gauge was maintained at the temperature of melting ice. The very sensitive differential manometer employed by Petterson in his apparatus for the determination of the carbonic acid in air might also find further application.

The manometer employed by Lord Rayleigh in the determination of the densities of gases is described on p. 127.

*Barometers.*—The common syphon barometer is too well known to require description.

A very convenient form of barometer (Fig. 83), which possesses the advantage of being very easily filled, has been described by

Collie (*Chem. Soc. J.*, 1895, 129). The stem of the instrument is sealed to the top of the cistern, which is in the same axis with it, and is continued to the bottom of the cistern by means of the capillary tube *a*, which is bent to one side. The cistern communicates with the air through the tube *b*; the trap *c* below the upper chamber serves to catch any minute bubbles of air that might find their way up the stem.

The instrument may be filled with mercury by the usual process of introducing small quantities of mercury and boiling to expel the air, or by the following method. The tube *b* is made rather long, and is drawn out to a long capillary about 0.5 mm. internal diameter. The tube is sealed to the pump and the instrument is exhausted as far as possible, while the glass is heated to remove moisture. The capillary tube can then be sealed, and by breaking the point beneath the surface of some mercury in a basin the barometer may be filled, leaving only an inappreciable trace of air in the upper bulb.

The presence of a minute trace of air has practically no influence upon the readings of the instrument, and, indeed, when the air has been completely expelled, the mercury adheres to the glass after the instrument has been tilted, and only by warming or shaking can be made to fall to the barometric height.

The readings are taken with reference to a scale placed behind the instrument. For absolute determinations of the barometric height in experiments on the densities of gases, etc., the scale should be compared with a standard of length.

*The temperature correction.*—Since both the density of mercury and the length of the scale change with temperature, each time the barometric height is read the temperature is taken, and a correction is applied in order to determine the true pressure. The correction may be applied by direct calculation in the following manner.

Suppose the scale to be of standard length at temperature *t*, and that the reading is taken at

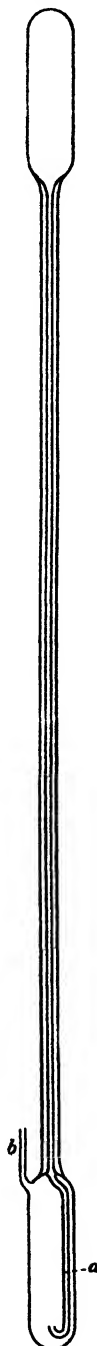


FIG. 88.

temperature  $t'$ , which may be taken as identical for scale and barometer.

If  $l$  is the observed reading at  $t$ , since a greater number of divisions will correspond to the same length at the lower temperature, the corrected reading will be  $l[1 + a(t - t')]$ , where  $a$  is the coefficient of expansion of the scale. If the scale is correct at  $0^\circ \text{C.}$ , and the temperature is expressed in degrees Centigrade, the corrected reading becomes  $l(1 + at)$ .

Similarly, if the corrected height of the mercury column alone becomes  $l_0$

$$l_0 = \frac{l}{1 + at} = l[1 - (0.000181 + a)t]$$

The coefficient  $a$  has the following values:—

For brass	0.0000188
For steel	0.0000104
For glass	0.0000091

The assumption that the scale is correct at  $0^\circ \text{C.}$  cannot as a rule be made.

A scale, from which the correction may be read off directly, may be constructed in the following manner (Fig. 84). The ordinates represent in millimetres the height of the mercury column, and the abscissæ the correction in terms of the same units. The correction for each alternate degree of temperature is represented by one of the diagonal lines; intermediate points may be obtained by interpolation. In constructing the scale, the values of the correction to be applied to a column of mercury are calculated from the equation—

$$\text{Correction} = l(\beta - a)t$$

The following values have been calculated for a barometer 800 mm. high with a glass scale correct at  $15^\circ \text{C.}$

8°	1.101	16°	2.201	24°	3.302
10°	1.376	18°	2.477	26°	3.578
12°	1.651	20°	2.752	28°	3.853
14°	1.926	22°	3.027	30°	4.128

J. Shields (*Phil. Mag.* May 1896) has described a mechanical device for determining the correction to be applied for temperature.

The instrument consists of a barometer of the Collie type, mounted in front of a mirror scale in such a manner that it can be given a vertical motion by means of a screw A. The mercury in the cistern is adjusted to the level of a zero line B, and the height of the column is read off on the scale which is ruled in millimetres between 700 and 800 millimetres from this point, the intervening space is left blank.

The attachment by which the temperature correction is applied, consists of a thermometer which is clamped to the stem of the barometer; the capillary is so bent that the portion C of

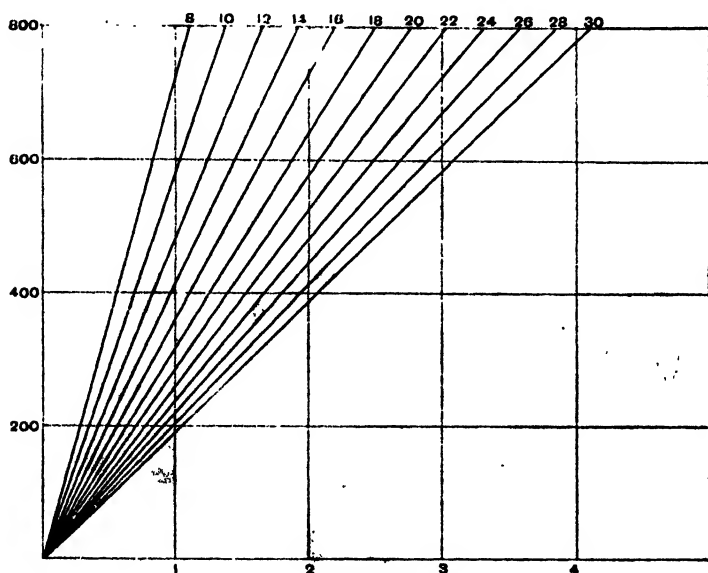


FIG. 84.

it which contains the end of the thread of mercury lies in a horizontal position in front of a scale. The thermometer moves vertically with the barometer when the mercury in the cistern is adjusted to the zero line, and consequently each position which it can occupy corresponds to a certain length of the mercury column. The correction is read off by determining the position of the end of the thread of mercury with regard to the horizontal divisions, which are naturally wider at the bottom than at the top, since they correspond to longer columns of mercury.

The method of ruling the scale requires some explanation. Since it is required to reduce the barometric height to  $0^{\circ}\text{C}$ ,





FIG. 85.

it is obvious that the zero line must be a vertical line corresponding to the zero of the thermometer. It is not necessary to determine the length in millimetres corresponding to 1 on the thermometer stem; suppose this to be  $n$  millimetres.

Since the distance through which the barometer is raised or lowered to set the level of the mercury in the cistern to the zero line, is one-half the distance that the barometer has risen or fallen since the last adjustment, a distance of 50 mm. between the upper and lower horizontal lines on the scale will correspond to a difference of 100 millimetres of barometric height. The length of the divisions 1, 2, 3, 4, can be found from the equation

$$c = l(\beta - \alpha)l$$

Substituting  $nt$  for  $l$  to obtain the length in millimetres, and 0.000172 if the scale is of glass.

One division of the upper line = 800 (0.000172)  $nt$ .  
 .. lower .. = 700 (0.000172) ..

These points are then joined by straight lines.

After setting up the instrument the position of the thermometer is adjusted without difficulty.

In barometers such as have been described there is no correction for capillarity, but in every case the instrument should be tapped with the finger before a reading is taken.

*Absolute normal pressure.*—Since the absolute normal pressure is expressed by the pressure exerted by a column of mercury 76 metre in height multiplied by the gravitation constant, it is necessary to apply a correction in order to compare observations taken in different latitudes, or at

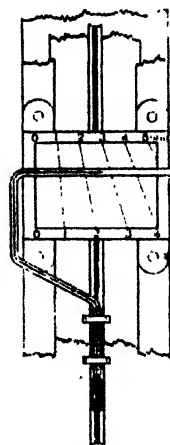


FIG. 86.

different heights above sea-level. The value of the gravity constant in latitude 45', which is taken as the standard, is 980.61. For the comparison of the densities of gases the Paris standard ( $g = 980.94$ ) has been employed (p. 128).

*Relation of temperature and volume.*—Although Dalton and Charles may be said to share the honour of the discovery of the law connecting volume and temperature, it is to Gay-Lussac and Humbolt that we owe our first definite knowledge of the subject. These two philosophers determined the coefficient for air under constant pressure, and later Gay-Lussac extended the observations to other gases, proving that the expansion was practically the same in every case (*A. de Ch. et de Ph.* I. 43, 137).

A glass bulb, sealed to a long capillary stem, was filled with mercury, and the gas was introduced so as to leave a pellet of mercury in the stem. The bulb was placed in a metal vessel, which could be filled with ice or boiling water, so that the stem projected in a horizontal position through the walls. The volume of the gas was indicated by the position of the pellet of mercury in the stem, which was graduated; the mean coefficient for air, corrected for the expansion of the glass, was found to be 0.00375.

This number was accepted as correct till 1830, when it was shown by Rudberg, a Swedish chemist, that the true value was near 0.00365, pointing out that in Gay-Lussac's experiments the bulb probably contained moisture. The measurements were made at constant volume.

As in the case of many other physical constants, the relationships of temperature, pressure, and volume were first accurately determined by Regnault. The increase of pressure at constant volume was determined by means of an apparatus consisting of a globe connected by a narrow tube with a mercury manometer. The mercury was brought to a mark on the manometer by means of a screw adjustment, and the difference of height of the mercury in the two limbs was measured directly. The bulb was immersed in ice or surrounded with steam; a correction was applied for the gas contained in the leading tube and in the top of the manometer, which remained at the temperature of the air.

In the determination of the volume expansion at constant pressure, the limb of the manometer, which was connected with the bulb, was graduated, and the volume of one division as well as that of the bulb and connecting tubes were known. The mano-

meter was maintained at constant temperature in a water-jacket, and at each reading the mercury was brought to the same level in both limbs. His results were as follows :—

	At constant Volume.	At constant Pressure.
Air . . . . .	0·003667	0·003670
Hydrogen . . . . .	0·003667	0·003661
Nitrogen . . . . .	0·003668	...
Carbon dioxide . . . . .	0·003688	0·003110

The results show that both the volume and pressure coefficients vary in the different gases, and that the two constants are not the same, even for a single gas. As might be expected, the difference between the two constants is of the same order and sign, as the variation of  $pv$  with  $p$  for any particular gas.

Regnault also determined the relative expansion of air and other gases by a differential method.

Of recent years more attention has been paid to the determination of the pressure coefficients, the determination of the increase of pressure produced by heating a gas at constant volume.

Von Jolly (*P. A.* 1874, *B.* 1880, 2019, 401, *C. r.* 106, 162) has obtained the following values for the pressure coefficients of the principal gases :—

Hydrogen . . . . .	0·0036562
Oxygen . . . . .	0·0036742
Nitrogen . . . . .	0·0036677
Nitrous oxide . . . . .	0·0037067
Carbon dioxide . . . . .	0·0037060

The values of the coefficient for air determined by Regnault, Magnus, and Jolly, corrected by Mendeléef (*B.* 10, 81), show a very close agreement. The mean, 0·0036700, may be taken as very near the true value.

The most accurate determinations of the pressure coefficients of hydrogen, nitrogen, and carbon dioxide that have yet been made are probably those of P. Chappuis of the Bureau International. The details of the experiments, which have been carried out in this institution, are described in Guillaume's *Thermometrie* and in the *Travaux et Mémoires de la comité internationale des poids et mesures*. The thermometer bulbs employed were made of platino-iridium :—

	Coefficient at 0° C.	Pressure at 0° C.
Hydrogen	0.0036624	1000 mm.
Nitrogen (atmospheric)	0.00367445	1000 "
Carbon dioxide	0.00372477	995 "
"	0.00371634	870 "

The *comité international* have adopted as a normal thermometric scale the constant volume hydrogen thermometer, having an initial pressure of 1000 mm. of mercury. On this scale the freezing and boiling-points of water are 273.04 and 373.04; and as it appears probable that the value of the pressure-coefficient is nearly independent of the temperature over a considerable range, a degree of temperature has the same value at any point of the scale. The volume-coefficient for hydrogen under similar conditions is found to be 0.0036600, which gives 273.2° as the freezing-point of water. The variation of the volume-coefficient with pressure is given by Amagat as

$$\frac{\delta\epsilon}{\delta p} = 0.00000186$$

per atmosphere.

Chappuis has compared the nitrogen thermometer with the normal hydrogen thermometer. The variation between 0° and 100° is insignificant, and at 500° C. amounts to 0.07°.

In order to illustrate the general principles of the method by which the pressure-coefficient of a gas may be determined, or by which temperature may be determined by means of a constant volume gas-thermometer containing a gas whose pressure-coefficient is known, some experiments carried out by Kuenen and Randall (*Phil. Mag.* 1895) will be described. The apparatus employed is shown in Fig. 87.

The bulb *a*, which was 120 mm. long and 22 mm. in diameter, was sealed to a capillary stem, and was connected through a stopcock with the

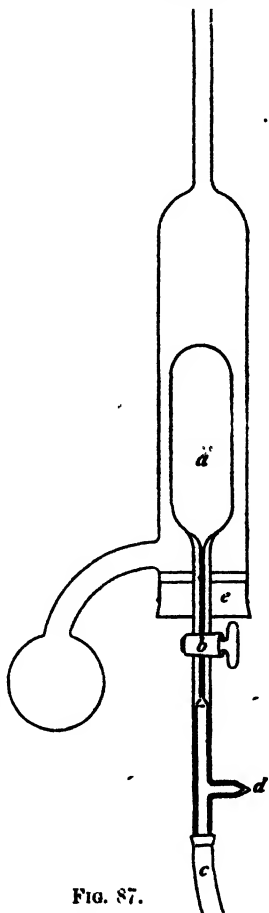


FIG. 87.

rubber tube *c*, leading to a mercury reservoir, and with an apparatus for the introduction of the gas (p. 300). The rubber stopper *c* was placed on the stem before it was sealed to the bulb.

The reservoir was first filled with mercury, and raised till the mercury rose to the level of the top of the rubber tube, the tube was then closed by means of a rubber pinchcock. The bulb was then exhausted, the gas introduced, and the side-tube *d*, which had previously been drawn out to capillary diameter, sealed in the blow-pipe flame. The pressure of the gas in the bulb at the ordinary temperature was about two-thirds of an atmosphere.

The bulb was first surrounded with melting ice and then heated in a Ramsay and Young vapour-jacket to the temperature of the vapour of certain pure liquids, of which the boiling-points were accurately known. The temperatures were controlled by a series of experiments in which the bulb of the thermometer was filled with air. The vapour-jackets were protected from air currents by means of a screen. The method of measuring the pressure on the gas consisted in bringing the mercury to a point on the wide tube above the tap and just below the capillary. The vertical height of the mercury column was read by means of a scale and telescope. Corrections were applied for capillarity, and for the temperature of the mercury.

The volume of the bulb was determined, and also the volume of the stem outside the vapour-jacket; the volume of the latter amounted to about  $\frac{1}{3000}$  of the whole; it was corrected for.

The volume expansion of the bulb was determined for another piece of the same glass by the weight thermometer method, the expansion was taken to be a linear function of the temperature.

The following results serve to indicate the accuracy of the method:—

	Freezing Point of Water.	Boiling Point of Water.	Coefficient of Expansion, 0 - 100.	Temperature Calculated.			
				Chloro-benzene.	Aniline.	Quino-line.	Bromo-naptha-line.
	Pressure in mm. of Mercury.						
Hydrogen . . . . .		712.56	...	131.6	183.9	236.35	...
Air (a) . . . . .		737.74	...	131.8	183.9	(234.9)	281.65
Helium, D 2.13 . . . . .	567.02	745.18	0.003665	132.2	184.1	236.9	...
Argon (a), D -19.99 . . . . .	517.02	706.06	0.003668	132.15	184.1	...	...
Argon (b) . . . . .	529.54	...	...	...	...	237.8	281.5
Air (b) . . . . .	511.68	698.79	0.003663	...	...	237.1	...
Ramsay and Young (C. S. J., 47, 640, 55, 483) . . . . .			...	132.1	184.4	237.4	280.4

The boiling-point of water was determined from the measurements of Kohlrausch.

The same instrument has been employed in the measurement of low temperatures by Olszewski and others; but though in many cases the results appear to be very concordant (p. 156), their absolute value may sometimes be questioned, since the correction to be applied for the volume of the gas in the part of the stem, which is not cooled, and for the contraction of the glass, are somewhat difficult to determine. Mr. Baly has determined the contraction of glass between the atmospheric temperature and  $-180$  with the following results:—

Volume coefficient about normal temperature . . .	0.0000285
„ between $0^{\circ}$ and $-150^{\circ}$ C. . .	0.0000219

The results show that the coefficient cannot be considered as constant down to the temperature of liquid air.

*The compensated constant-pressure gas thermometer.*—In order to eliminate the correction for the uncooled portion of the stem of the thermometer, Cullendar (*Proc. Roy. Soc.* 50, 247) has introduced an instrument which I shall describe in detail, as it is capable of giving results of the highest accuracy. The thermometer is of the *constant pressure* type, the pressure of the gas being adjusted, and the volume measured at each experiment. The instrument, which is shown in Fig. 88, consists of two parts, B a burette connected by the capillary tube *a* with the thermometer bulb A; and a bulb C, also sealed to a capillary

tube *b*, which is of the same dimensions as, and is bent similarly to *a*. The two parts of the instrument are connected to the two limbs of the differential manometer *D*. The readings are taken by measuring the volume of gas in the burette after adjusting the level of the mercury till the pressure in the two parts of the apparatus, as indicated by the differential manometer, are equal.

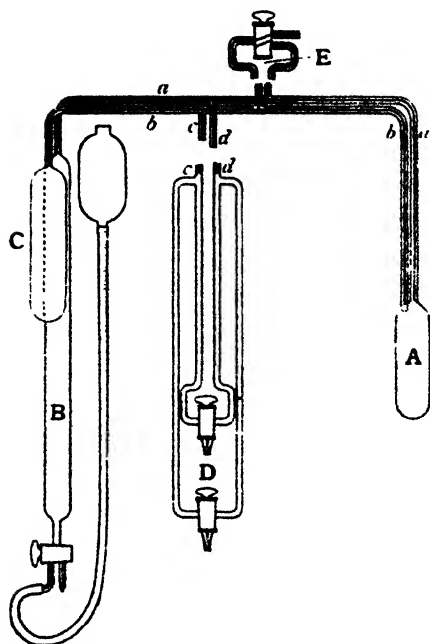


FIG. 88.

The conditions under which compensation is perfect are very simple. They are—(1) That the two sets of connecting tubes, the burette *B* and the bulb *C*, should be at the same mean temperature; (2) that the mass of gas in the two parts of the instrument should be the same; (3) that the pressures should be adjusted to equality.

Where  $V_c$  = volume of air in bulb *C*,  
 $m_c$  = mass of air in bulb *C*,  
 $\theta_c$  = temperature of air in bulb *C* on the air scale,  
 $p_c$  = pressure of air in bulb *C*,  
 $v$  = volume of connecting tubes,  
 $\theta$  = temperature of connecting tubes on the air scale,

$$p_c \left( \frac{V_c}{\theta_c} + \frac{v}{\theta} \right) = mk,$$

where  $k$  is a constant.

$V_t$  = volume of air in thermometric bulb *A*, and  $\theta_t$  its temperature.  
 $V_m$  = volume of air in mercury burette *B*, and  $\theta_m$  its temperature.  
 $m_t$  = mass of air in thermometric bulbs and burette.  
 $p_t$  = pressure of air in thermometric bulbs and burette

$$p_t \left( \frac{V_t}{\theta_t} + \frac{V_m}{\theta_m} + \frac{v}{\theta} \right) = mk.$$

And since  $m_t = m$  and  $p_t = p_n$ ,

$$\frac{V_t}{\theta_t} + \frac{V_m}{\theta_m} = \frac{V_n}{\theta_n}.$$

By keeping the standard pressure bulb B and the burette at the same temperature  $\theta_n$ ,

$$\theta_t = \frac{V_t \times \theta_n}{V_n - V_m}.$$

It remains to give a detailed description of the construction of the apparatus and the method of using it. The dimensions of the bulbs A and C will, of course, depend upon the purpose to which the instrument is to be applied. When employed as an air thermometer in measuring temperatures not far distant from the normal, when the bulb is immersed in a liquid which is well stirred or which is boiling, a capacity of 50 c.c. is a convenient dimension. In the measurement of low temperatures, and in cases in which it is difficult to maintain a considerable space at the same temperature, the bulb should be much smaller. The range of the instrument will also depend upon the relative sizes of the bulbs, for if the bulb A is not considerably smaller than the bulb C, it will be impossible in measuring low temperatures to adjust the pressure on the two sides of the instrument to equality by allowing mercury to enter the burette, the two masses of gas being equal to one another.

The manometer is shown in the figure detached from the rest of the apparatus so as to make its structure clear. The tubes *c* *d* are connected with two U-tubes of about 1.5 mm. diameter which lie in the same vertical plane. The tubes are sealed to two-way stopcocks, so that they can be filled with sulphuric acid and mercury respectively after the apparatus has been exhausted and the gas introduced. The vertical limbs of the inner U-tube, which contains the sulphuric acid and by which the final adjustment of the pressure is made, lie as close to one another as possible. The outer U-tube contains mercury, and is employed in roughly adjusting the pressures to equality; it may be dispensed with if the adjustment is made by means of a mercury reservoir attached to the burette by a rubber tube.

The apparatus may be exhausted, and the gas introduced by means of a two-way stopcock E, connected with both sections of



the instrument which, for convenience, may also communicate through a second stopcock.

The burette B may be graduated, and the readings ( $V_m$ ) may be observed directly by means of a telescope. In this case the burette is connected, through a stopcock and piece of rubber tube, with a mercury reservoir, and the sulphuric acid is brought to a level in the two limbs of the U-tube by raising or lowering it. More accurate measurements can, however, be made by filling the burette with mercury to a point on the capillary tube, and running the mercury into a weighed vessel till the pressures are brought to equality. The volume  $V_g$  is obtained from the weight of the mercury, the mercury manometer being used in the first instance for the adjustment of the pressure. If the burette is connected by one tube of a two-way stopcock with a mercury reservoir, it can at once be refilled with mercury for a second observation. It is of course necessary to turn the two stopcocks on the sulphuric acid and mercury gauges during this operation to prevent the acid or mercury from being forced into the bulb C.

The apparatus may be set up as indicated in the figure. The burette and the bulb C are enclosed either in an air space between sheets of glass, in a water-jacket, or in a vessel containing melting ice; the temperature  $\theta_0$  is read on a thermometer placed between them. The connecting tubes may be covered with cotton wool.

The operation of filling the instrument with gas may be carried out in the following manner. The apparatus is first exhausted and allowed to remain in connection with the pump for some time to remove traces of moisture, and to show whether it is perfectly gas-tight. It is then filled with pure air, or with hydrogen from palladium (p. 43), and before the stopcock connecting the two sections of the apparatus is closed the level of the mercury in the burette is set so that the volume of each section is the same, and the whole apparatus is left to itself in a room in which the temperature is constant. If a very high degree of accuracy is desired, the burette and the compensating and thermometer bulbs are surrounded with melting ice. The stopcock can then be closed.

*The absolute scale of temperature.*—The terms, absolute zero and absolute temperature, introduced by Lord Kelvin in 1848, are somewhat loosely used, and without going far into the question

it may be well to say a word or two with regard to their significance.

In the simple gas equation

$$PV = RT$$

the temperature,  $T$ , is reckoned from the zero of the perfect gas thermometer, and if the degree of temperature be arbitrarily defined as one-hundredth part of the difference between the melting-point and boiling-point of water under normal pressure, these points will lie close to  $273^{\circ}$  and  $373^{\circ}$  on the absolute scale (see p. 149).

As far as is at present known, or is indeed possible on theoretical considerations, no gas obeys exactly the simple laws. Consequently, if the value of a degree of temperature is maintained, the absolute temperatures of the melting and boiling-points of water will only approximate to the temperatures expressed on the scale of a gas thermometer. To determine the exact relationship between a gas scale and the absolute scale of temperature, a complete knowledge of the thermo-dynamic properties of the gas would be necessary. The relationship of temperature, pressure, and volume should be determined over a considerable range, and the Joule-Thomson effect (p. 188), which gives in a sense a measure of the perfection of the gas, should be known. Unfortunately, in the cases of hydrogen and helium, we have no accurate knowledge whatever in this direction. In the first case the gas employed has always been very impure, and in the second no experiments have yet been attempted. It appears probable that helium and hydrogen approach very nearly to the perfect gas, since the value of  $pv$  for them appears to vary only very slightly from the normal over a considerable range of pressure. Olszewski's observation that the readings of constant-volume thermometers filled with hydrogen and helium agree exactly down to the boiling-point of liquid oxygen suggests that in neither case is the difference between the gas scale and the absolute scale of any magnitude. It is highly improbable that if any great divergence occurred it would be the same in both cases.

In these experiments Olszewski employed two constant volume thermometers of 10 c.c. capacity. The following figures indicate the nature of the agreement between the results, though

they must only be taken as comparative, and not as direct, measurements of temperature.

Vapour pressure of liquid.	Temperature by helium thermometer.	Temperature by hydrogen thermometer.
741	- 182.6	- 182.6
240	191.8	191.85
90.4	- 198.7	198.75
12	- 209.3	209.2
9	- 210.57	210.6

It may be added that helium approaches most nearly to the ideal thermometric substance, and, indeed, furnishes the *only* means of measuring accurately temperatures about and below the boiling-point of hydrogen. For such purposes the helium must have been freed from argon or other gases of higher boiling-point. Further, since the gas cannot undergo dissociation at high temperatures, and does not pass through the wall of a red-hot platinum vessel, as does hydrogen, it may also be applied to the measurement of high temperatures.

For the actual measurement of temperature it appears probable that the constant-volume thermometer gives results which approximate to the absolute temperatures. According to Van der Waals, the pressure-coefficient at constant volume is independent of the temperature, the equation

$$p = \frac{R}{v-b} T + \frac{a}{v^2} \quad (\text{p. 177})$$

becoming

$$p = kT,$$

in the case of the more permanent gases under normal pressure. Though this is not strictly true for high temperatures it is probable that the deviations at low temperatures are of a lower order than the errors of experiment.

*Abnormal expansion.*—In the majority of cases, as has already been pointed out, the pressure-coefficient between 0° and 100° is practically constant. It must not be forgotten, however, that this is not the case with gases whose boiling-points are not far below zero. Sulphur dioxide shows a considerable variation in the pressure-coefficient (Amagat, *C. r.* 73, 183).

0° - 10°	.	.	.	0.004233
10 - 20°	.	.	.	0.004005
50°	.	.	.	0.003846
100	.	.	.	0.003756

V. Mayer and Langer (*Pyrometrische Untersuchungen*, 1885, and *B.*, 1885, 1501) have shown that at high temperatures sulphur dioxide and nitrogen do not show the same expansion. It would appear that under these conditions the polyatomic gases, and perhaps even the diatomic gases, dissociate.

*The relationship of temperature, pressure, and volume in rarefied gases.*—Until recently no method has been devised for the determination by direct measurement of the pressures exerted by rarefied gases, and, indeed, when the pressure becomes equal to a column of mercury less than two or three millimetres in height, it becomes difficult to obtain accurate or concordant observations.

*The McLeod gauge.*—This instrument (Fig. 89) was designed with a view to measuring the pressure exerted by rarefied gases. The cylinder A, which terminates in a closed capillary tube C, is connected through the trap E with the apparatus under exhaustion through the tube D, and with a mercury reservoir attached to B. The capillary is graduated and calibrated, and the capacity of the apparatus to the lower opening of the trap is known; the tube D is also graduated. The whole apparatus may, if necessary, be enclosed in a water-jacket.

In taking a reading the reservoir is raised so that the mercury rises in A and D, forcing the gas contained in A into the capillary. Between measurements the level of the mercury is kept just below the trap. It is found that if the mercury is allowed to fall any distance below the trap when the reservoir is raised air is drawn through the trap into the chamber A. The volume of the gas is then read off, and the pressure on it is directly determined from the difference of level of the two columns of mercury.

If it were possible to make the assumption that the law

$$p_1 v_1 = p_2 v_2$$

holds good over wide differences of pressure, since the initial and final volume and its final pressure are known, it would be possible to calculate its initial pressure, and it is only on this assumption that the McLeod gauge serves to measure pressure. It does, however, serve to determine the volume of gas

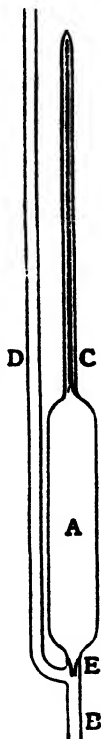


FIG. 89.

measured at normal temperature and pressure which fills a partially exhausted space.

The relationships of temperature, pressure, and volume of rarefied gases, and the efficiency of the McLeod gauge, were made the subject of a thorough investigation by Professor Ramsay and Mr. E. C. C. Baly; a historical *resumé* of the subject will be found in their paper. With regard to the McLeod gauge, it was found to be utterly untrustworthy as a means of measuring low pressures in the case of air or carbon dioxide. It appeared that considerable surface condensation took place, and that the magnitude of the error so introduced varied not only with the extent of the surface exposed to the gas, but with the nature of the glass: no two gauges ever gave comparable results. With hydrogen, however, the case was different. Perfectly concordant readings were obtained, and by comparing the readings of the McLeod gauge with the pressures indicated by a manometer, it was found that for pressures between 650 and 2.5 millimetres of mercury *pv* had a constant value.

As it was found impossible to observe with any accuracy pressures smaller than 2.5 millimetres, no direct evidence that the value of *pv* at lower pressures remained constant could be obtained. By measuring the quantity of gas in an apparatus of known volume after a known number of strokes of a pump of known capacity it appeared, however, that the expansion was quite regular, and that no surface condensation took place down to a pressure of 0.000076 millimetres. Consequently, when working with pure hydrogen, and probably also with helium, neon, argon, etc., the McLeod gauge may be depended upon to a certain extent.

With carbon dioxide marked indications of surface condensation were observed, and after a time further pumping did not appear to reduce the pressure, which had apparently become equal to the vapour pressure of the condensed gas. This result was confirmed by admitting a known volume of carbon dioxide to the exhausted apparatus, and observing the pressure recorded by the McLeod gauge.

It may be well to mention here the curious anomaly first observed by Bohr in the expansion of oxygen. At 0.7 mm. the pressure becomes erratic, and it is quite impossible to obtain

concordance between two consecutive readings till some days have elapsed. It would appear that some intrinsic change takes place, probably dissociative, and some time is required for equilibrium to be established. The gas behaves regularly at lower pressures.

The coefficient of expansion was determined by jacketing one of the two gauges with the vapour of a boiling liquid. The following is a summary of the results.

(i.) The coefficient of expansion of hydrogen is normal down to 0.1 millimetres; at lower pressures it decreases.

(ii.) The coefficient of expansion of oxygen is greater than the normal. It increases to  $2\frac{1}{3}$  at 1.4 millimetres: at 0.7 millimetres it becomes erratic, but appears to increase steadily at lower pressures.

(iii.) The coefficient of expansion of nitrogen is lower than the normal at pressures between 1 and 5 millimetres; it decreases at lower pressures.

At the close of their paper, Messrs. Baly and Ramsay discuss the probability of a limiting value to the pressure exerted by a rarefied gas. On the basis of the kinetic theory gas pressure is assumed to be caused by impact of the molecules upon the walls of the containing vessel, and when energy is communicated to the gas it is partially transformed into internal and partly into translational energy. It is possible to conceive of a condition of rarefaction in which the whole, or nearly the whole, of the energy is transformed in the molecule itself, giving rise perhaps to the phenomena allied to phosphorescence. In the gas equation " $p$ " would then assume a lower limiting value; such a condition would obtain in the limiting layer of the atmosphere.

Lord Rayleigh (*Proc. Roy. Soc.* 1901) refers to an apparatus for the direct measurement of very low pressures; the details have not yet appeared. His results appear to show that the value of " $pv$ " remains constant in the case of the commoner gases down to very low pressures, and he failed to observe the irregularity in the expansion of oxygen at a pressure of about 7 mm.

*For the molecular weight of gases at low pressure, see p. 140.*

*The exhaustion of glass apparatus.*—In the exhaustion of glass apparatus it is necessary to take into consideration the condensation of gases and of moisture on the surface of the glass. In order to eliminate any chance of the presence of hydrocarbons, or

of any quantity of carbonic acid, the apparatus should be thoroughly cleaned before it is attached to the pump. After sealing the apparatus to the pump it should be partially exhausted, and allowed to stand for a time in order to permit of the absorption of water vapour by the pentoxide of phosphorus. During the latter stages of the exhaustion a few moments should be allowed to elapse between each stroke of the pump, in order to allow time for the equalisation of the pressure throughout the apparatus.

It has already been pointed out that after a time, if the apparatus contains carbon dioxide, a limit of exhaustion is reached. For the production of high vacua it is necessary to thoroughly heat the vessel under exhaustion either with a Bunsen burner or by enclosing it in an asbestos oven. The carbon dioxide may be "washed out" of the apparatus by admitting a small quantity of pure air and re-exhausting. The exhaustion of glass apparatus will be dealt with further in the chapter on spectrum analysis.

## CHAPTER XIV

### RELATIONS OF TEMPERATURE, PRESSURE, AND VOLUME OVER WIDE RANGES OF PRESSURE AND TEMPERATURE

Boyle's law—Despretz's experiments—Pouillet's experiments—Dulong and Arago—Regnault's experiments, the value of  $pv$  at constant temperature—Natterer's experiments—Cailliet's experiments—Amagat's experiments and the application of his results—Kammerlingh Onnes' standard manometer—Observations of Cagniard-Latour—Andrews' investigations—The critical state.

FROM the time of the discovery of the law connecting pressure and volume by Boyle and Mariotte about the year 1666 up to 1837, its absolute value had remained unquestioned. In that year Desprézt succeeded in showing that at a pressure of fifteen atmospheres hydrogen was less compressible than carbon dioxide and sulphuretted hydrogen. He employed a differential method. The gases were confined over mercury in similar tubes, which were enclosed in a glass vessel containing water; the pressure was applied by means of a screw piston. The method was afterwards improved by Pouillet, who first employed the metal compression chamber and screw plunger; the capillary tubes containing the gases projected through the wall of the chamber.

Dulong and Arago were the first to apply the direct pressure of a column of mercury to the compression of gases, but their results failed to indicate any deviation from Boyle's law.

Later, Regnault undertook the study of the compressibility of gases, and in a long series of experiments succeeded in determining the deviations from Boyle's law with considerable accuracy. Regnault's results have now been superseded, but they are of considerable historical importance, and served with sufficient accuracy as a basis for his researches on the specific heats of gases and in other investigations.

Regnault's apparatus closely resembled that of Dulong and



Arago. The manometer consisted of a series of thick-walled glass tubes joined in to a height of 30 metres, and set at their base into an iron vessel, which was also in communication with the tube containing the gas, and with a force-pump. The pump, which was intended to transmit pressure to the mercury in the iron chamber by means of water, could be cut off by means of a stopcock when an observation was being made. This was essential on account of the inconvenience caused by leakage.

Since the negative results obtained by Arago and Dulong might be accounted for by the fact that when the gas is compressed to small volume, the error of observation becomes a considerable part of the whole, and comparable with the deviation to be sought for, Regnault devised another method. The compression tube was not sealed at the top, but was connected by means of a stopcock with a vessel containing the gas to be examined under pressure. There were two divisions on the manometer tube marking equal volumes from the stopcock. The method of observation was as follows.

The compression tube and manometer were filled with mercury, and gas was admitted till the mercury fell to the level of the first mark; the stopcock was then closed, and the pressure was adjusted and observed. The pressure was then allowed to fall until the gas had expanded to fill the tube to the second mark, and a second observation was taken. In this way it was possible to obtain a series of relative values of  $p$  $v$ , and eliminating such errors as might be connected with the measurement of volume, the accuracy of the manometer readings was about 0.5 mm. It was necessary to apply corrections for the temperature of the mercury column, and for the barometric pressure at the surface of the mercury.

Regnault's results proved conclusively that in the majority of cases the compressibility was greater than was stated by Boyle's law. In the case of hydrogen, the "*gas plus que parfait*," it was less (see also p. 197).

The relationship of pressure and volume over wide ranges of pressure was first studied by Natterer. The results of his investigations are published in the *Sitzungsberichte der Wiener Akademie* and in *Poggendorf's Annalen* between the years 1844 and 1855. The gas was compressed into a wrought-iron vessel by means of a pump, and the pressure was transmitted through

mercury to a loaded piston, which acted as a manometer. The lower surface of the piston was hollowed, and the edges, turned to razor sharpness, formed a thin ring of metal, which was pressed by the liquid against the walls of the cylinder, forming a good joint. This arrangement, which had previously been employed in experiments on liquids under pressure, was afterwards modified by Amagat, and applied to the measurement of very high pressures. Natterer's results can only be taken as pointing qualitatively to a divergence from Boyle's law in the case of all the gases examined.

Caillaud, to whom much of our knowledge concerning the compressibility and liquefaction of gases is due, also conducted a series of researches on the same subject. In his earlier experiments the gas was confined in a compression tube (Fig. 98), and the pressure was applied by turning a screw, as in Pouillet's apparatus. The pressure was measured by reading the rise of mercury in the stem of a thermometer with a spherical bulb which was contained inside the apparatus. In his later experiments the tube which contained the gas was completely enclosed in a steel vessel, which was connected through a long, flexible steel tube with an open reservoir containing mercury. The tube was wound on a drum 2 metres in diameter, fixed on a vertical axis, and the case containing the compression tube was lowered into an artesian well. On the inside of the glass compression tube a thin film of gold had been deposited, which was dissolved by the mercury, and served to indicate the volume to which the gas had been compressed. The pressure was determined by measuring the vertical height of the mercury column in the steel tube. This amounted in some cases to 500 metres of mercury:—

"   
 VALUE OF  $p_v$  AT 200 ATMOSPHERES FOR AIR

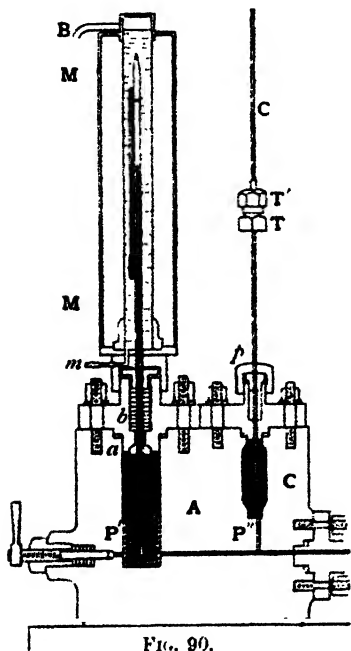
Natterer	.	.	.	.	.	.	.	1.01
Caillaud	.	.	.	.	.	.	.	1.05
Amagat	.	.	.	.	.	.	.	1.07

It appears probable that the results obtained by Amagat for the compressibilities of nitrogen, oxygen, air, and carbon dioxide are most to be relied upon. The experiments were commenced in 1878, and the results are to be found in the *Comptes rendus* (1878, **87**, 438; 1879, **88**, 336, **89**, 436; 1884, **99**, 1153).

The experiments are described in detail in the *Annales de Chimie et de Physique* (1880, **19**, 345; 1881, **22**, 353; 1883, **28**, 456, 464). A *resumé* of his researches was published in the same journal in 1893.

Amagat's method was similar to that of Régnault, only the tube which formed the manometer was of steel, joined in sections to a height of 330 metres in his later experiments. The apparatus was first set up at Lyons on the face of a cliff above the Saone. Later it was removed to the shaft of a coal-pit at Verpilloux near St. Etienne, where it was possible to obtain a vertical height of 340 metres.

A section of the apparatus is shown in Fig. 90. The gas was contained in the glass compression tube A, the capillary portion MM of which passed through the cap of the compression chamber, leakage being avoided by packing the space *b* with greased leather washers. The capillary tube MM was surrounded by a water-jacket, and a current of water entering at *m* and escaping at B maintained it at constant temperature. The spaces P' P'' inside the apparatus contained mercury, and communicated through a screw-down cock with a strong iron vessel, also containing mercury, into which glycerine could be pumped. In this way the mercury was forced to rise in the steel tube C, which entered the apparatus through the cap *p*. The tube was of about 2 millimetres internal diameter, and the sections of it, which were about 25 metres long, were



connected by screw unions, and secured by clamps to the iron pipe which supplied air to the lower galleries of the mine.

The capillary portion of the glass compression tube was graduated; it was about 50 centimetres long and 1 millimetre internal diameter. To eliminate errors in observation, due to the small volume occupied by the gas at high pressures, three tubes

of different capacities were employed. The tubes were capable of withstanding a pressure of 500 atmospheres, but their actual expansion under high pressures was not determined.

In making an experiment it was necessary to mount in the cage to the height at which an observation was to be taken. One of the unions between two sections of the steel tube was then unscrewed, and the upper tube was replaced by a cap carrying a glass cylinder. Then mercury was thus raised by the pump below till it entered the glass vessel, and readings of the volume of the gas and of the vertical height of the mercury column were taken simultaneously. The height of the barometer at the upper level, and the temperature of the mercury, as indicated by thermometers placed 30 metres apart, were also determined. The latter only varied very slightly, as there was but one shaft to the mine. The vertical heights were measured by means of a steel wire, and were afterwards referred to a scale 10 metres long. The extension of the wire was also determined.

These experiments form the basis of nearly all modern experimental work involving the measurement of high pressures, and from this point of view they are of the highest importance. The relationship of pressure and volume at  $15^{\circ}$  C. were only determined directly by means of the apparatus just described in the case of atmospheric nitrogen, which was very rightly taken as the standard gas. The results obtained with oxygen, air, and carbon dioxide are none the less reliable, but in the case of hydrogen the gas was obviously impure. Amagat states that the gas was obtained by heating together oxalic acid and soda lime; formic acid was probably used, and in this case the gas would contain at least 20 per cent of carbon monoxide. On the basis of these results Sarrau calculated the critical constants of the gas by means of Van der Waals' equation.

NITROGEN.—(a) The values of  $PV$  at pressures between 30 and 430 atmospheres were determined by means of the open manometer in 1880. The results are expressed in terms of an empirical value of  $PV$  at 30 atmospheres. (b) The values of  $PV$ , in terms of  $PV$  at normal pressure equal to unity, between 20 and 65 atmospheres determined by a similar apparatus erected in a church tower at Fourviers in 1884.

The following table contains the values of  $PV$  for nitrogen at  $15^{\circ}$  C. between normal pressure and 220 atmospheres. The

values at 5, 10, and 15 atmospheres are obtained from Regnault's observations. The values of  $PV$  at the higher pressures have been reduced from Amagat's empirical values, which are given in italics. The agreement between the two series is very good.

### SERIES I. (*b*).

P metres <sup>3</sup> .	PV.	P metres <sup>3</sup> .	PV.
0.76	1.0000	35	0.9899
5	0.9981	40	0.9896
10	0.9963	45	0.9895
15	0.9946	50	0.9897
20	0.9930	55	0.9902
25	0.9910	60	0.9908
30	0.9908	65	0.9913

### SERIES II. (*a*).

P.	PV relative .	PV/V at 0.76 m. = 11.
<i>29.740</i>	<i>50989</i>	<i>0.9924</i>
<i>35.337</i>	<i>50897</i>	<i>0.9908</i>
40	...	0.9898
45	...	0.9891
<i>47.146</i>	<i>50811</i>	<i>0.9891</i>
50	...	0.9892
55	...	0.9898
60	50687	0.9906
<i>61.241</i>	<i>50895</i>	<i>0.9910</i>
65	50939	0.9915
<i>69.140</i>	<i>50687</i>	<i>0.9925</i>
70	...	0.9927
75	...	0.9941
80	...	0.9958
<i>82.970</i>	<i>51226</i>	<i>0.9971</i>
85	...	0.9978
90	...	0.9993
95	...	1.0018
<i>96.441</i>	<i>51602</i>	<i>1.0045</i>
<i>96.698</i>	<i>51594</i>	<i>1.0043</i>
100	...	1.0066
110	...	1.0148
120	...	1.0233
<i>128.296</i>	<i>52860</i>	<i>1.0301</i>
130	...	1.0314
140	...	1.0397
150	...	1.0480
<i>158.563</i>	<i>54214</i>	<i>1.0552</i>
160	...	1.0566

P.	PV (relative).	PV (V at 0.76 m. = 1).
170	...	1.0655
180	...	1.0752
190	...	1.0860
190.885	55850	1.0871
200	...	1.0970
210	...	1.1055
220	...	1.1207
221.103	57796	1.1250

When these results are plotted it is noticed that the value of  $pv$  at first decreases, and attains a minimum at about 55 metres. Between 65 and 100 metres the value of  $pv$  increases very rapidly, and between these limits manometer readings would not indicate the pressure with any great accuracy.

*Relationship of pressure and volume for air at 15°.*—The values of  $pv$  between 20 and 65 metres, expressed in terms of the value at atmospheric pressure, are taken from Amagat's latest paper (*C. r.*, 1884, 1153). The values at 5, 10, and 15 metres were calculated from Regnault's results by Prof. Sydney Young, who also points out that the figure 0.9832 for the value of  $pv$  at 35 metres is probably incorrect; the true value obtained by three methods of interpolation appears to be 0.98365. The values of  $pv$  for pressure above 65 metres are taken from Amagat's earlier results (*A. de Ch.*, 1880, 375); they were obtained by comparing the nitrogen and air manometers. The values of  $pv$  in the second series are reduced to the same standard,  $pv$  at atmospheric pressure equal to unity, from the relationships of the interpolated values at 55, 60, and 65 metres. The agreement between the two series is good, although in the second series the temperature was 22°.

#### SERIES I.

P (metres).	PV.	P (metres).	PV.
0.76	1.0000	35	0.98365
5*	0.9977	40	0.9824
10*	0.9951	45	0.9815
15*	0.99255	50	0.9808
20	0.9901	55	0.9804
25	0.9876	60	0.9803
30	0.9855	65	0.9807

From Regnault's measurement.

## SERIES II.

P (metres .	PV (relative .	PV	PV at 0.7
47.25	26791		9811
50	.		9811
55	.		9810
57.50	26798		9810
60	.		9807
64.00	26778		9806
65	.		9806
70	.		9809
72.16	26792		9811
84.22	26840		9829
101.47	27041		9903
133.89	27608	1.0110	
177.60	28540	1.0452	
214.54	29585	1.0810	

The apparatus employed in determining the compressibilities of air, oxygen, etc., only differed from the one described on p. 164 in that in the place of the open manometer, the chamber containing the compression tube was connected with a second steel vessel containing a compression tube filled with nitrogen to act as a gauge, and a screw plunger was employed to facilitate the final adjustment of the pressure. Two nitrogen manometers were used, one indicating pressures below 130 atmospheres, the other pressures above 100 atmospheres. So as to make certain that the two sets of results were strictly comparable, both manometers were placed at once in the compression apparatus, and readings were taken between 100 and 130 atmospheres. In determining the compressibility of a second gas the, mercury in the nitrogen manometer was always brought to a point at which an actual observation had been made against the open manometer.

The effect of temperature on the compressibility of gases was also investigated; in some cases a series of isothermals were determined.

Amagat has also determined the relationships of temperature, pressure, and volumes up to 3000 atmospheres. The methods employed are described in the *resumé* of his more important researches in the *Annales de Chimie et de Physique* for the year 1893. The values of  $V$  and  $PV$  corresponding to every 100 atmospheres up to 3000 atmospheres are given at 0, 16, and 45° for hydrogen, nitrogen, and air, and at 0 and 16 for

oxygen; the volumes at 3000 atmospheres pressure, in terms of unit volumes under standard conditions, for these gases are as follows:—

	Volumic.	t.
Oxygen .	0.0012960	15.6
Hydrogen .	0.0010125	15.4
Nitrogen .	0.0015225	16.0
Air .	0.0014660	15.7

The values of  $V$  and  $PV$  for the same gases corresponding to every 50 atmospheres up to 1000 atmospheres is also given at 0, 16, 100, and 200 C.

For a description of the method employed reference must be made to the original paper; it will suffice to state here that the pressure applied to the surface of a large piston was transmitted through a piston of much smaller area in the same axis, to the liquid in the apparatus containing the gas. From the pressure at the surface of the large piston, and the ratio of the areas of the two pistons, the pressure on the gas could be directly calculated.

A shortened form of the open manometer was suggested by Andr ws, and has recently been applied by Kammerlingh Onnes (Netherland's Academy, 1898, "Communications from the Physical Laboratory of the University of Leyden," No. 44) to the measure-

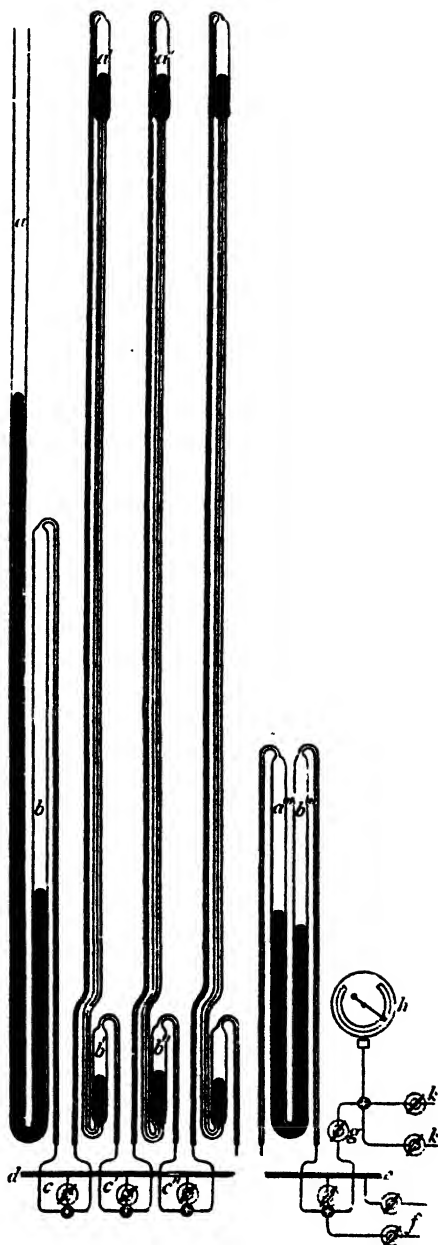


FIG. 91.



ment of high pressures. A number of glass syphon manometers,  $ab$ ,  $a'b'$ ,  $a''b''$ , etc., are placed in series, the upper chamber of each being connected with the cistern of the next, and also, through a steel cock,  $c$ ,  $c'$ , with a tube  $de$ . The first syphon,  $ab$ , of the manometer is of the same diameter throughout, is open to the atmosphere, and serves for the measurement of small fractions of an atmosphere; a short U-tube  $a''b''$  at the high pressure end of the system serves a similar purpose. The tube  $de$  is connected through a cock  $f$ , with a cylinder filled with compressed air, through a cock  $g$ , with a Bourdon gauge  $h$ , and through the cock  $k$  or  $k'$  with any piece of apparatus in which the pressure is to be determined. The gauge serves to indicate the pressure to which the manometer must be adjusted before the cock  $g$  is opened.

The manometer tubes  $a'b'$ , etc., are of such a length as to give a difference of level of 3.04 metres (4 atmospheres) between the surfaces of the mercury; to withstand the higher pressure the thickness of the walls of the wider portions was 4 mm., and the internal diameter 6 mm. The connections are made by means of fine steel tubes and caps fitting over the ends of the steel tubes, and the cocks  $c$ ,  $c'$  are also of steel. In order to preserve the apparatus the air was carefully dried before it was allowed to enter by passing through cylinders containing soda lime and pentoxide of phosphorus.

The adjustment of the apparatus to a given pressure is performed by admitting air cautiously into the spaces between columns of mercury. To bring the pressure to  $46\frac{1}{4}$  atmospheres, for instance, it will be necessary to raise the mercury to the full height in 10 of the syphons,  $b$ ,  $b'$ , etc., and to the height corresponding to  $2\frac{1}{4}$  atmospheres in the open tube  $ab$ . To do this the cocks  $c$ ,  $c'$ , etc., are all opened and the cock  $f$  on the air cylinder is turned till the mercury rises in  $ab$  to the required height;  $k$  and  $c$  are then closed. By again opening the cock  $f$  the mercury is raised to the full height in the syphon  $a'b'$ , and after closing  $c'$  in each of the syphons in turn till the pressure in the tube  $de$  has reached  $46\frac{1}{4}$  atmospheres. After opening the cock  $g$  any small final adjustment can be made by means of the short U-tube.

The heights of the columns are read off on graduated rods suspended between the manometers, the temperature of each column is determined by means of a thermometer placed beside it.

In determining the pressures from the observed heights, it is necessary to subtract the weight of the columns of air in the connecting tubes between the levels of the meniscus in two adjacent syphons. In the case of air this connection amounts to 120 mm., when the pressure is raised to 60 atmospheres.

The instrument is chiefly employed in standardising compression manometers.

The compressibility of hydrogen at low temperature has been determined by Wroblewski (*Wiener Akademie*, 1888), but the observation only covered a limited range. He found that the equation, which is similar in form to that of Clausius,

$$p = \frac{RT}{V - a} - \frac{K}{\epsilon^2 - V^2}$$

held good between  $+100^\circ$  and  $-182^\circ$  C. He gives the following values for the constants:  $R = \frac{1}{273}$ ,  $a = 0.0011695$ ,  $K = 0.00051017$ ,  $\epsilon = 1.003892$ .

*The effect of temperature on the compressibility of gases.*—The researches of Regnault did not extend to the determination of the compressibility of gases at temperatures other than  $0^\circ$  C. Between 1862 and 1866 Van der Kolk determined the relative compressibilities of several gases at  $0^\circ$  and  $100^\circ$  C. (*Pogg. Ann.* **116**, 427, **126**, 433). The results showed that whereas the compressibility of air did not vary between these temperatures, the deviation from the *pv* law was less in the case of carbon dioxide at  $100^\circ$  than at  $0^\circ$ . Amagat in 1871-72 (*C. r.* **73**, 184, **75**, 179) obtained similar results over wider ranges of temperature.

In 1822 Cagniard-Latour had observed that when a liquid was heated in an enclosed space it became totally vaporised above a certain temperature. He employed the apparatus shown in Fig. 92. The branch *a* of the U-tube contained air and served to measure the pressure exerted by the vapour of the liquid in *b*. The apparatus was heated in an air-bath, the temperature of complete volatilisation was determined, and the pressure was calculated from the volume of the air in the tube *b*. He obtained the following results:—



FIG. 92.

	Temperature of volatilisation.	Pressure.
Ether . . . . .	175° C.	38 Atm.
Carbon bisulphide . . . . .	258 ..	71 ..

He was unable to completely volatilise water. It is interesting to note that the numbers do not lie very far from the actual critical temperatures and pressures of these liquids.

As has already been pointed out, it was the results of the researches of Andrews which explained the failure of Faraday, Natterer, and others to liquefy the so-called permanent gases by pressure alone. Faraday, indeed, appears to have regarded the permanent gases as being in a state comparable to that of the ether in Cagniard-Latour's experiment; but though he believed in the existence of a critical temperature he made no attempt to confirm this view by experiments on the gases that he had actually liquefied. The results of Andrews' first experiments were published as a note in Miller's *Chemical Physics* in 1863, and are stated as follows:—"On partially liquefying carbonic acid by pressure alone, and gradually raising at the same time the temperature to 31° C., the surface of demarcation between the liquid and the gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striae throughout the entire mass. At temperatures above 31° C. no apparent liquefaction of carbonic acid, or separation into two distinct forms of matter, could be effected, even when a pressure of 300 or 400 atmospheres was applied, nitrous oxide gave analogous results." The temperature at which the phenomenon took place he called the critical point. This observation formed the basis of a series of investigations, and the results, under the title "The continuity of the gaseous and liquid states," was made the subject of the Bakerian Lecture for the year 1869 (*Phil. Trans.*, 1869, 575). The following is a brief account of his experiments.

The gases were contained in glass tubes *a, b, c, d* (Fig. 93). The tubes were of capillary bore from *a* to *b*, the section *bc* was 2·7 mm. in diameter, and the section *cd* somewhat smaller. The capillary tubes were carefully calibrated, the capacity of one millimetre of length being from 0·000025 to 0·000030 c.c., the volume of the apparatus from some point on the capillary tube

to two marks  $e$  and  $f$  were also known. These marks served to determine the volume of the gas confined over mercury in the tube, after the point  $a$  had been sealed, by determining the change of pressure required to bring the surface of the mercury from  $e$  to  $f$ .

The tubes were filled with the gases to be examined by attaching the end  $d$  to the apparatus generating the gas, and allowing a stream of gas to pass through the tube for some time. The tube was then sealed close to  $a$ , and the end  $d$  was temporarily closed.

The end of the tube  $d$  was opened beneath the surface of mercury in a vessel so arranged that the pressure on the surface of the mercury could be reduced by means of an air pump. During this operation gas escaped from the tube, and on restoring the pressure mercury entered to take its place. Some of this mercury was afterwards removed from the tube, so that the gas

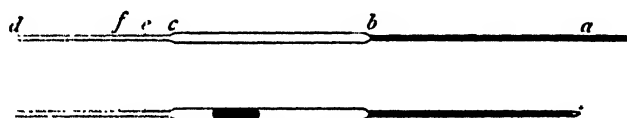


FIG. 93.

was finally confined in the upper portion of the tube by means of a plug of mercury (Fig. 93). The tube was then attached to one limb of a long U-tube containing mercury, and the pressure exerted by the gas when the mercury was brought to the points  $e$  and  $f$  was determined. The volume of the gas was calculated from these data.

Two tubes which contained respectively air, and some other gas such as carbon dioxide, were placed in the same compression apparatus which was of the form employed by Pouillet. The compression chamber, a rectangular box of stout copper, contained the wider portions of each tube, the capillaries alone projecting through the top. The chamber contained water, and the pressure was applied by means of two screws which passed through glands into the interior.

The capillaries were surrounded by water-jackets: the one containing air was maintained at nearly constant temperature, the other at temperatures which varied between  $13^{\circ}$  and  $48^{\circ}$ .

The tube containing air served as a manometer, but since

the deviations from Boyle's law were not known with sufficient accuracy, the results were expressed as if the equation  $PV = c$  were absolutely true.

The most important experiments, which form the subject of the Bakerian lecture, were carried out with carbon dioxide. But since the gas contained about  $\frac{1}{500}$  of its volume of air the results are not of the highest accuracy. This, however, does not detract from their importance.

The results are most easily explained by means of the curves shown in Fig. 94.

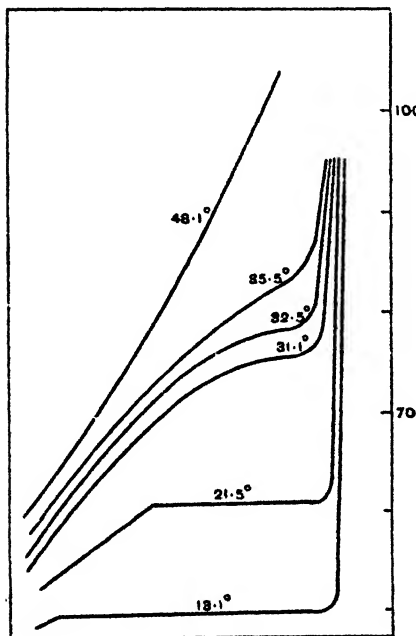


FIG. 94.

When carbonic acid was compressed at 13.1 the volume decreased regularly till a pressure of 49.1 atmospheres, as indicated by the air manometer, was reached. At this point liquefaction commenced, and if the gas had been quite free from air, the whole of the gas would have liquefied without further increase of pressure; this change would have been represented by a portion of the curve parallel to the lines of equal pressure. It was found that the increase of pressure required to liquefy the first and second-thirds was only 0.25 atmospheres, but to liquefy the whole of the gas an increase of pressure of 1.5 atmospheres was required. This can be fully accounted for by the presence of air.

The curve representing the relationship of pressure and volume at 21.5° has the same form as the first; the pressure required to produce liquefaction, and the final volume of the liquid were, of course, greater.

It was noticed that the compressibility and thermal expansion of liquid carbonic acid were considerable; the latter observation was first made by Thilorier.

The next set of experiments were conducted at temperatures above the critical point,  $30.92^{\circ}\text{C}$ . The results showed that in each case a considerable reduction of volume occurred after arriving at a certain pressure, but although the "flickering movements" due to change of density in different parts were observed, no separation of liquid took place. The change of volume is shown by the curves to be less abrupt when the temperature lies farther from the critical point: at  $48^{\circ}\text{C}$ . it has disappeared altogether.

These results lead to the conclusion that the gaseous and liquid states are only widely separated forms of matter, and that the changes from one to the other take place without interruption or breach of continuity.

*The equations of Van der Waals and others.*—From the study of the relations of temperature, pressure, and volume, even over limited ranges, it is obvious that the equation,

$$PV = RT,$$

is only an approximation, even for the more perfect gases at temperatures distant from their critical points.

That Regnault succeeded in applying an empirical formula to the results which he had obtained has already been pointed out, but even if his observations had been of a more accurate nature his formula could not have held over wider ranges. Further, from the true gas equation it should be possible to calculate the critical constants as well as the isothermals.

A formula based on physical considerations as to the constitution of gaseous matter must necessarily take into consideration the size of the molecules and their mutual actions and attractions. The most remarkable attempt to develop an equation of this kind was made by Van der Waals in an inaugural dissertation in 1873.

The idea first put forward by Andrews, that there is no breach of continuity between the gaseous and liquid states forms the basis of the theory of Van der Waals. In both cases we must consider the constituent molecules under the influence of *internal* forces dependent upon their character and proximity. The molecules in the mass of the substance must be acted upon equally in all directions, while on those in the *surface* the attraction tends only to draw them inwards.

If the attraction of molecules in a small element of the surface on each molecule within the substance, is proportional to the products of their masses, or to some similar property independent of the temperature, since the number of molecules in unit surface or in unit volume is proportional to the pressure, the attraction will vary inversely as the square of the volume. The value of  $P$  in the gas equation then becomes  $(P + \frac{a}{v^2})$ .

Taking into consideration the volume of the ultimate particles,  $V$  becomes  $(V - b)$ , where  $b$  is the volume occupied by the gas when compressed to the utmost. The value of  $b$  was supposed by Van der Waals, on the basis of the theory of probabilities, to be four times the actual volume of the molecules. According to O. E. Meyer it should be  $4\sqrt{2}$  times the volume; this number has been verified by Young from his observations on the alcohols. The gas equation then becomes:—

$$(P + \frac{a}{v^2})(v - b) = RT.$$

This formula was first applied to the recalculation of the isothermals of carbon dioxide from the experimental results of Andrews, with satisfactory results; but the range of the experiments was not sufficiently wide to serve as a crucial test. Before, however, going further into the question of its validity, it may be well to point out a few general facts with regard to it.

The equation represents the value of  $PV$  as decreasing at first, attaining a minimum and then steadily increasing. This is obvious since  $\frac{a}{v^2}$  increases more slowly as  $v$  decreases, and  $(V - b)$  only begins to differ appreciably from  $V$  when the latter becomes small.

In the case of hydrogen the experiments of Joule and Thomson in 1854 had shown that on expanding the gas without interference of external pressure, no rise of temperature was observed as in the case of other gases, but, if anything, a cooling effect, and that consequently the internal attraction among the particles was practically zero. As Regnault's experiments have shown, the value of  $PV$  increases directly with the pressure and does not show a decrease at first.

When applied to gases near their critical points the iso-

thermals exhibit the irregularities first demonstrated by Andrews; and at temperatures below the critical point the following rather remarkable results are obtained.

Andrews' curves show that on reaching a certain pressure, dependent on the temperature only, liquefaction commences, and becomes complete without further change of temperature or pressure. There are thus two volumes corresponding to these conditions, the volume of the gas, and the volume of the liquid. As James Thomson subsequently pointed out, relationship of pressure and volume about the point of liquefaction should be represented by a sinuous line *abcde*, and not by the straight line *ace*.

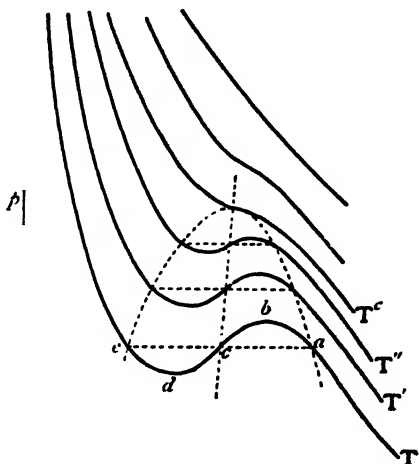


FIG. 95.

Since Van der Waals' formula is an equation of the third degree, it has either one or three real roots, and gives instead of two volumes three, the third (p. 249) being situated between the other two. The curve is sinuous and of the form *abcde*. Of the physical meaning of this third volume, or of the portion of the curve *bcd*, we can have no conception; the curve *ab* represents supercooled vapour, and the curve *dc* superheated liquid.

At higher temperatures the three points representing the three volumes come closer together, till they finally coincide in the critical point. At this point, therefore, the three roots of the equation become equal; the calculation of the volume of the critical constants is not difficult.

If the initial pressure and volume be made equal to unity,

$$R = \frac{PV}{T} = \frac{(1+a)(1-b)}{273}$$

$$\left(P + \frac{a}{V^2}\right)(V-b) = \frac{(1+a)(1-b)}{273}.$$



Solving for  $V$ ,

$$V^3 - \left\{ b + \frac{(1+a)(1-b)T}{273P} \right\} V^2 + \frac{a}{P} V - \frac{ab}{P} = 0,$$

which is an equation of the form,

$$V^3 + xV^2 + yV + z = 0.$$

If its three roots are  $p$ ,  $q$ , and  $r$ ,

$$(V - p)(V - q)(V - r) = 0.$$

And since the three roots become equal at the critical point, if  $\phi$  is the critical volume,

$$V - \phi = 0.$$

If  $\theta$  is the critical temperature, and  $\pi$  the critical pressure,

$$(V - \phi)^3 = V^3 - \left\{ b + \frac{(1+a)(1-b)\theta}{273\pi} \right\} V^2 + \frac{a}{\pi} V - \frac{ab}{\pi}.$$

And since corresponding coefficients of  $V$  must be equal,

$$\phi = \frac{ab}{\pi}, \quad 3\phi^2 = \frac{a}{\pi}, \quad 3\phi = b + \frac{(1+a)(1-b)\theta}{27\pi}$$

$$\phi = 3\pi, \quad \pi = \frac{a}{27b^2}, \quad \theta = \frac{8}{27} \frac{a}{Kb}.$$

The calculated value of the critical point of carbon dioxide was  $32.5^\circ$ ; it was not, however, possible to trace the isothermals far by means of this formula.

In Van der Waals' equation it is assumed that the value of  $a$  is independent of the temperature, and that  $b$  is also a constant; in the latter case it appears probable that the variations with temperature and pressure are not great. The first attempt to connect the value of  $a$  with the temperature was made by Clausius, who put forward the equation,

$$\left( p + \frac{K}{T(\epsilon + \beta)^2} \right) (v - b) = RT.$$

The equation has no direct physical meaning, as  $K$  and  $\beta$  are arbitrary constants, and it does not represent the form of the isothermals with greater accuracy than the equation of Van der

Waals. The results obtained by Young for the relations of temperature, pressure, and volume for isopentane led Rose-Innes (*Proc. Roy. Soc.* **15**, 126, **16**, 11) to the following formula,

$$p = \frac{R\tau}{v} \left\{ 1 + \frac{a}{v+k} - \frac{b}{v^2} \right\} - \frac{l}{v(r+k)}$$

This equation is of the fifth order, but since it has only three real roots it is capable of expressing the relationships about the critical point.

Quite recently Dieterici (*Wied. Ann.* **69**, 685) has put forward a suggestion that the term  $a$  in Van der Waals' equation does not vary with  $v^2$  but with  $v^{\frac{2}{3}}$ ; the reasoning is as follows:—Let us imagine a slice, of an area of one square centimetre, cut from the middle of the substance in the critical state, the slice being so thin that only one molecule can lie in it. Let  $n$  be the number of molecules in volume  $v$ , then  $\frac{n}{v} = N$  are present in one cubic centimetre. Let us suppose with Clausius that each molecule be surrounded by a cube of edge  $\lambda$ .

$$\frac{n}{v} \lambda^3 = N \lambda^3 = 1 \text{ c.c.}$$

A slice of height  $\lambda$ , and of one square centimetre in area contains  $N^{\frac{2}{3}} = \left(\frac{n}{v}\right)^{\frac{2}{3}}$  molecules.

The cohesion pressure  $\pi$ , which is expressed by  $\frac{a}{v^2}$  in Van der Waals' equation, is the sum of all forces exerted by molecules contained in the slice. Assuming with Van der Waals that this force is inversely proportional to the volume, we have

$$\pi = \left(\frac{n}{v}\right)^{\frac{2}{3}} \frac{c}{v}$$

where  $c$  is a constant;

or

$$\pi = \frac{a}{v^{\frac{5}{3}}}.$$

We might proceed to test the truth of this conclusion by determining whether by introducing the term  $\frac{a}{v^{\frac{5}{3}}}$  in place of  $\frac{a}{v^2}$  in Van der Waals' equation, we obtain an equation which expresses

both the form of the isothermals, and the values of the critical constants for any gas. The equation becomes

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

$$\frac{bp + RT}{p}v^3 + \frac{a}{p}v - \frac{ab}{p} = 0,$$

an equation of the form

$$\alpha x^3 + \beta x^2 + \gamma = 0,$$

and which can only have three real roots

$$v_c = 4b, \quad p_c = \frac{a}{4(4b)^2}, \quad T_c = \frac{15ab}{4(4b)^2R}.$$

$$v_c = 4b, \quad p_c = \frac{a}{4v_c^2}, \quad T_c = \frac{15ab}{4Rv_c^3}.$$

From this we arrive at the numerical relationship deduced by Young,

$$\frac{RT_c}{p_c v_c} = 3.75.$$

It is interesting to calculate the nature of the ratio obtained by replacing  $\pi$  by expressions involving different powers of  $v$ .

$\pi$	$\frac{RT_c}{p_c v_c}$
$\frac{a}{v^3}$	$\frac{48}{7} = 6.89$
$\frac{a}{v^4}$	$\frac{15}{4} = 3.75$
$\frac{a}{v^5}$	$\frac{8}{3} = 2.66$
$\frac{a}{v^6}$	$\frac{21}{10} = 2.10$
$\frac{a}{v^7}$	$\frac{96}{55} = 1.75$

So far we have only considered the value of  $b$  close to the critical point, and as we know from Van der Waals' dissertation, from Boltzmann's analysis of it, and from the work of Clausius, that it is not quite independent of the temperature and pressure, and that at great pressure it becomes only a small multiple of

the co-volume. If  $b_{\infty}$  is its value at great rarefaction, Boltzmann places

$$(r - b) = \frac{r}{1 + \frac{b_{\infty}}{r} + \frac{5}{8} \left( \frac{b_{\infty}}{r} \right)^2 + \text{etc.}}$$

but at the same time the limits of variation will probably not be greater than as 1 to 10. Actually determined values of  $b$  are a little uncertain, as they are always obtained as differences between large numbers.

An attempt has been made to determine more exactly the nature of the variation in  $b$ , without much success, and the equation, like that of Van der Waals and Clausius, does not exactly express the form of the isothermals over wide limits.

It will probably be found that the cohesion pressure is not a purely mechanical one, and, as in Clausius' equation, is a function of  $T$ . These questions have been discussed in a recent paper (*Wied. Ann.*, 1901, [iv], 4, 51).

## CHAPTER XV

### THE LIQUEFACTION OF GASES

The experiments of Davy and Faraday—Thilorier's experiments on carbon dioxide—The liquefaction of oxygen by Pictet and Cailletet—The researches of Olszewski, Wroblewski, Dewar, and Onnes—Isothermal and adiabatic expansion—Free expansion, the Joule-Thomson effect—Application of the principle of free expansion by Hampson and Linde—The production of liquid air by Hampson's apparatus—The liquefaction of hydrogen.

AN account of the earlier attempts to liquefy gases is to be found in any text-book of physics or chemistry, and it would serve no useful purpose to enlarge upon it here. The later history of the subject is, however, of the highest importance, more particularly with regard to the production of liquid air, and its application to research at low temperatures. Without reference to questions of priority I shall describe those researches which have resulted in the introduction of new processes, or in the application of new principles to the liquefaction of gases.

In the experiments of Davy and Faraday the gases were generated in closed glass tubes of the form shown in Fig. 96. The



FIG. 96.

substance from which the gas could be obtained was placed in one limb of the tube, which was then sealed. The gas condensed in the other limb of the tube, which was cooled to about  $-20^{\circ}$  C. in a freezing mixture.

These experiments resulted in the liquefaction of all the commoner gases, with the exception of hydrogen, nitrogen, oxygen,

methane, carbonic oxide, and nitric oxide. Faraday's views with regard to the nature of these so-called permanent gases have already been referred to.

In 1834 Thilorier employed a similar method for the liquefaction of carbon dioxide. The gas was generated by the action of sulphuric acid upon carbonate of soda, in a stout copper vessel connected with a second vessel in which it could be condensed. In this way he obtained a considerable quantity of the liquid, and by allowing it to escape through a jet into a box of non-conducting material he obtained the solid. Thilorier's observation, that a mixture of carbonic acid and ether formed a much more efficient refrigerant than the solid alone, was a valuable contribution to the experimental side of the subject.

After Thilorier's experiments, though many attempts were made to liquefy the permanent gases by pressure alone (p. 163), no further progress was made till 1877, when independent communications were submitted to the French Academy by M. Raoul Pictet of Geneva, and by M. Lewis Cailletet of Chatillon-sur-Seine, announcing the liquefaction of oxygen. In neither case was the liquid obtained in the static condition; but as the methods employed by the two investigators were new in principle and totally different, their work must be considered as of the very highest importance.

Pictet employed the method of *continuous cooling* by means of a volatile refrigerant; a method which he had successfully applied to the production of ice on a large scale. A diagram of his apparatus is shown in Fig. 97. The oxygen was generated in a steel retort *a*, connected with a steel tube *c*, which was surrounded by a

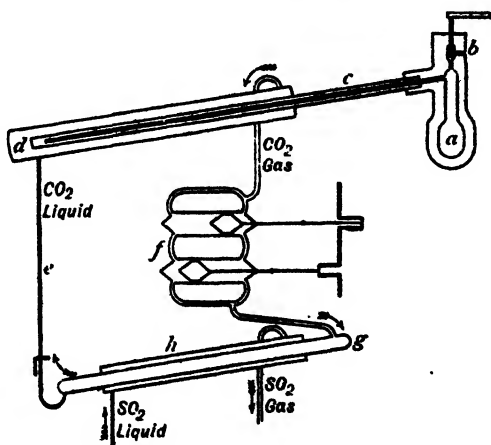


FIG. 97.

copper vessel *d*. Carbonic acid was condensed by means of the pump *f* into *g*, and allowed to flow through the tube *c* into *d*, where it was evaporated by means of the same set of pumps.

The system *djhc* formed a closed circuit: the liquid carbonic acid solidified in *d*, and the temperature produced by its evaporation reached  $-140^{\circ}$  C. The carbonic acid gas was cooled and condensed by means of sulphur dioxide, which was circulated through a similar closed system connected with the condenser *h*.

After working for many hours at fifteen horse-power the cock *b* was opened, and the pressure, which had risen to 320 atmospheres, was allowed to fall suddenly, producing an even greater degree of cold. On tilting the apparatus it was found that liquid oxygen was actually present.

Cailletet employed an apparatus (Fig. 98) similar to that of Pouillet (p. 161), in which the pressure was transmitted to the gas through mercury by means of a pump. The gas was compressed into the capillary portion of the glass tube under a pressure of 400 atmospheres; on releasing the pressure the sudden expansion resulted in the partial liquefaction of the gas, which appeared as spray or mist in the tube.

The researches of Pictet and Cailletet paved the way for the production of liquid air in quantity, and its introduction as an agent of research. The work has been carried out by Wroblewski and Olszewski in Cracow, by Dewar in England, and by Kammerlingh Onnes in Leyden; each of these investigators has worked on different lines, and their researches must in the main be considered independently. The Polish chemists devoted themselves chiefly to the determination of the boiling-points, vapour pressures, and critical constants of liquefied gases. Un-

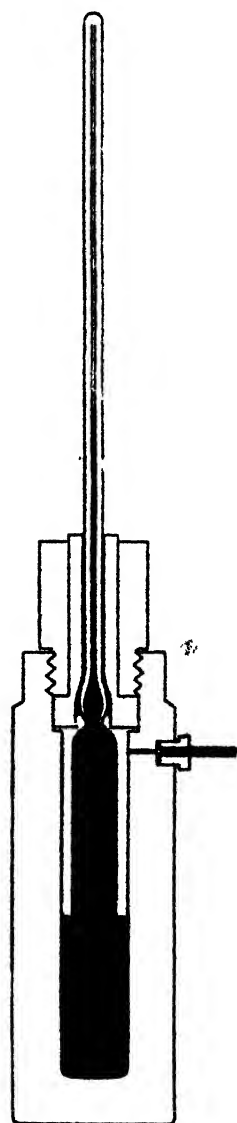


FIG. 98.

fortunately Wroblewski employed, in many of his researches, the thermo-electric junction for the measurement of temperature; but Olszewski's observations, in which the hydrogen (or helium)

thermometer was generally applied, are of the highest value. Dewar has devoted himself to the study of the chemical and physical properties of substances generally at low temperatures. These three investigators share the honour of having first devised practical methods for the production of liquid air in quantity, by the use of liquid ethylene in a system similar to that of Pictet.

The apparatus employed by Kammerlingh Onnes in his cryogenic laboratory in Leyden has been fully described by him in a series of papers, which have been translated into English from the *Proceedings of the Netherlands Academy*. The plant consists of a Pictet double cycle, employing methyl-chloride and ethylene as refrigerants. The system is not designed to produce liquid air in quantity at minimum cost, but to give a complete range of temperature down to  $-210^{\circ}\text{C}$ . Prof. Onnes' researches include the determination of the variation of a number of physical constants over wide ranges of temperature; among these may be mentioned the dielectric constants, and compressibilities of numerous gases.

The principle of adiabatic expansion involved in Cailletet's method may be briefly stated as follows. The gas is either compressed over mercury in a glass vessel and suddenly allowed to expand, or is allowed to escape from a steel vessel\* in which it is contained under pressure. In the first case, the gas does work in forcing down the mercury; in the second, the gas which remains in the vessel does work in forcing the remainder through the opening. In either case the gas in doing *external* work loses energy, and consequently if no heat is received from the outside it becomes cooled.

The specific heats of a gas at constant pressure or at constant volume, denoted by the symbols  $C_p$  and  $C_v$ , are defined as the quantities of heat required to raise the temperature of unit mass of the gas, at constant pressure or at constant volume, one degree Centigrade. Their values, in the case of a perfect gas, should be independent of the temperature and pressure.

If unit mass of gas is heated so that its temperature rises from  $T$  to  $T + dt$ , the pressure  $p$  remaining constant, the volume will increase from  $v$  to  $v + dv$ , and the quantity of heat absorbed in the process will be

$$C_p dt.$$

If the gas is now compressed isothermally to its original



volume  $v$ , the pressure will increase from  $p$  to  $p + dp$ , the work done will be represented by

$$vdp,$$

and in order to restore it to its original conditions of temperature and pressure, it will only be necessary to cool it down at constant volume, removing from it a quantity of heat  $C_v dt$ .

Since the cycle is now complete,

$$\begin{aligned} C_v dt &= C_p dt - vdp, \\ &= C_p dt - RT \frac{dp}{p}, \\ C_p - C_v &= R. \end{aligned}$$

If we now consider the first two processes in this cycle as taking place adiabatically, the gas undergoing a change of pressure from  $p$  to  $p + dp$  without loss or gain of heat :

$$C_p dt - RT \frac{dp}{p} = 0.$$

Replacing  $R$  by  $(C_p - C_v)$ , and dividing by  $T$ .

$$\begin{aligned} C_p \frac{dt}{T} - (C_p - C_v) \frac{dp}{p} &= 0, \\ \log_e T^p &= K, \quad \text{or} \quad T^p = K, \\ \log_e p^{(C_p - C_v)} &= \log_e K, \end{aligned}$$

where  $K$  is a constant.

The change of temperature resulting in a change of pressure is expressed by

$$(i) \quad \frac{T_0}{T_1} = \left( \frac{p_0}{p_1} \right)^{k-1}$$

where

$$k = \frac{C_p}{C_v} \text{ (see p. 271).}$$

By employing a similar thermodynamic cycle in which the gas is first heated at constant volume : secondly, allowed to expand isothermally at constant pressure ; and finally cooled at constant pressure to the initial conditions, we can obtain the relationship between temperature and volume during adiabatic expansion.

$$(ii) \quad \frac{T_0}{T_1} = \left( \frac{v_1}{v_0} \right)^{k-1}$$

From these two equations we find that for adiabatic expansion

$$pv^k = \text{Constant},$$

just as for isothermal expansion

$$pv = \text{Constant}.$$

If a gas were allowed to expand *without doing work*, it follows that no temperature change would occur; and, indeed, no *appreciable* effect is noticed when a gas is allowed to expand from one vessel into another which is exhausted; both vessels being immersed in a calorimeter.

These remarks apply, however, to a gas which rigidly follows the simple gas law,

$$pv = RT,$$

but they cannot be extended to any known cases, since in dealing with these we have to take into consideration not only the energy absorbed in performing external work, but also in overcoming internal molecular attractions, which the simple law does not consider.

The problem was first studied by Joule and Lord Kelvin (Joule and Thomson) in the following manner. A steady stream of gas, heated to a definite temperature by passage through a copper spiral immersed in a water-bath, was allowed to flow through a plug of silk fibre of such a thickness that there was no appreciable change in the velocity, and consequently in the kinetic energy, of the stream of gas in passing from one side of the plug to the other. Under these conditions work was done only in overcoming friction in the plug, the heat generated being absorbed by the gas, which would otherwise be cooled. The difference of temperature on the two sides of the plug, which was negative except in the case of hydrogen, could be attributed to absorption of heat by the gas in overcoming molecular attraction. Their experiments led them to the equation,

$$dt = K \frac{dp}{T}.$$

This phenomenon is known as the Joule-Thomson effect, and has been made the subject of more than one investigation.

The Joule-Thomson experiment may be graphically represented in the following manner:—The gas contained in the cylinder A

is forced through the plug or aperture B by the piston C, which in the actual experiment may be considered as moving in the stream of gas. The piston, in moving from *a* to *b*, expels *v*

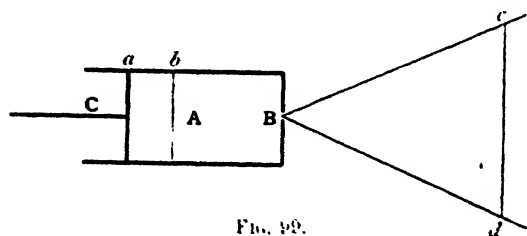


FIG. 99.

volume of gas from the cylinder, the pressure *p* remaining constant. The work done in overcoming the friction in the plug will be expressed by the product *pr*.

In the ideal experiment there is supposed to be no increase in the kinetic energy of the escaping gas, and its pressure is reduced to the external pressure *p'*. Since, however, it occupies a volume *v'*, represented by the area *Bed* in the diagram, which is larger than *v*, the heat absorbed will be expressed by *p'v'*.

In the case of a perfect gas

$$pr = p'v' ;$$

or the heat absorbed during the expansion is exactly equivalent to the heat generated by the friction in the plug and absorbed by the gas, and consequently the gas undergoes no temperature change.

In the case of an imperfect gas, however,

$$pr = p'v' + Q,$$

where *Q*, which is either positive or negative, expresses the heat change attributable to internal work.

The value of *Q* cannot be determined except by direct experiment, but it is possible to connect the equation given by Joule and Lord Kelvin with the modified equation. Rose-Innes has shown that from Van der Waals' equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

it is possible to derive an expression connecting the variation of *θ*, the Joule-Thomson effect, with *T*, the absolute temperature of the gas :

$$\theta = \frac{a}{T^2} \mp \beta,$$

where  $a$  is a function of  $a$  the internal attraction, and  $\beta$  is a function of  $b$  the co-volume (p. 176).

It is not surprising to find that closer relationship can be obtained from Clausius' equation,

$$\left[ p + \frac{a}{T(v+c)^2} \right] (v-b) = RT,$$

in which the intramolecular attraction is made to vary with the temperature as well as with the volume. The expression (Love, *Phil. Mag.* 1899) closely resembles that obtained by Joule and Lord Kelvin, but in the case of air the second constant vanishes.

$$\theta = \frac{\gamma}{T^2} + \delta.$$

The constants  $\gamma$  and  $\delta$  are functions of  $a$  and  $b$  respectively. The equation agrees very well with the results obtained by Natauson (*Wied. Ann.* xxxi. 502) for carbon dioxide.

The following values, expressed in degrees per atmosphere pressure, were obtained by Joule and Lord Kelvin for air and hydrogen.

	T	$\theta$
Air . . . . .	17.1	- 0.255
" . . . . .	91.6	- 0.203
Hydrogen . . . . .	6.8	+ 0.089
" . . . . .	90.3	+ 0.046

In the case of hydrogen, Joule and Lord Kelvin's results appear to have been somewhat inconclusive, and have not since been repeated. They certainly show that the effect was in the opposite sense to that in the case of the other gases which they studied, the gas heating instead of cooling on free expansion.

The variations of the Joule-Thomson effect over wide ranges of temperature and pressure have yet to be studied. The variations with temperature would be a matter of comparative simplicity; but to determine the temperature change in the gas resulting from a fall of pressure of 150 atmospheres would be a matter of considerably greater difficulty. In their original experiments Joule and Lord Kelvin found that when they employed great differences of pressure, the observed fall of temperature varied according as the thermometer was placed close to or far from the plug. In these experiments it appeared that the resistance of

the plug could not easily be made so great that the velocity, and consequently the kinetic energy, of the issuing gas was not increased in passing through it. The increase in the kinetic energy of the issuing gas necessitates an absorption of heat, so that there would be a fall of temperature close to the second surface of the plug, implying a conversion of molecular kinetic energy into translational energy of the mass of gas. This fall of temperature, which may be termed *velocity cooling*, would disappear at a short distance from the plug, the velocity of the stream of gas being reduced by friction with the walls of the tube or with the gas in the vessel into which it flows, resulting in the formation of eddies; the kinetic energy of the stream of gas would thus be reduced to its original value. The effective cooling of the gas is the result of the internal work only, though the velocity cooling which takes place close to the plug or valve, through which the gas is escaping, may result in a fall of temperature greater than could be accounted for by the Joule-Thomson effect; the velocity cooling would, however, be confined to a very limited region.

The application of this principle to the production of low temperatures has been successfully accomplished by C. Linde in Germany and by W. Hampson in England. These two investigators share the honour of having first succeeded in utilising the Joule-Thomson effect, and in obtaining liquid air without employing liquid ethylene or any other refrigerant. Linde's apparatus is probably the more effective for the production of liquid air in quantity; but it is much more cumbersome than Hampson's machine, and cannot be used for the production of a small quantity of liquid air in a short time. Hampson's apparatus is most suitable for experimental work; I shall therefore describe it.

The sectional diagram (Fig. 100) shows the arrangement of the installation at University College, London. Air is drawn into the compression pump through a cylinder A, which contains moist slaked lime spread upon trays. The pump, which is a torpedo-compressor manufactured by Whitehead and Co. of Fiume, compresses the air in two stages to 160-180 atmospheres,<sup>1</sup> the working pressure. In the first cylinder B the pressure is raised to about 16 atmospheres, and after passing through a copper coil C, the compressed air is delivered to the second cylinder D, where it

<sup>1</sup> The engineering unit of pressure, the atmosphere, is equal to 15 lbs. per square inch or 1 kilo. per square centimetre.

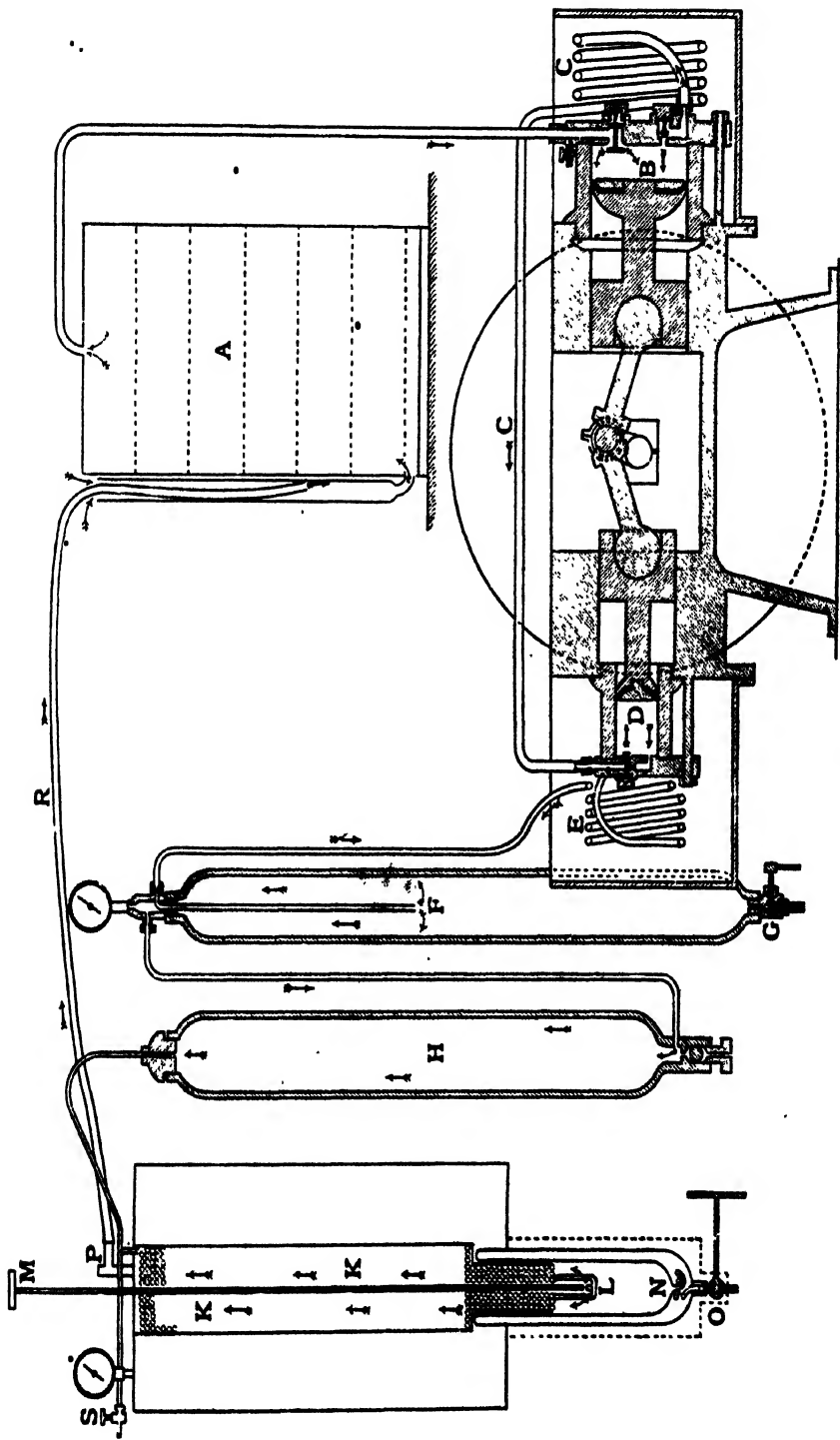


FIG. 100.

undergoes further compression, and after passing through a second copper coil E is delivered to the water-separator F; both the cylinders and the copper coils connected with them are contained in tanks through which water circulates to absorb the heat generated by the compression of the air. The compressor is worked by a five-horse-power electric motor. It can be worked in either direction: and since the mechanism is so arranged that the cylinders lie in the same axis, there is little vibration or noise.

In order to prevent the vulcanised fibre, with which the pistons are packed, from burning, and to lubricate the working parts, a little water is taken with the air into the low-pressure cylinder. The water, after passing through the high-pressure cylinder, finds its way into the water-separator and can be blown off from time to time by opening the cock G at the bottom of the latter. A certain quantity of water is also deposited from the saturated air on compression; and since the quantity of water vapour present is dependent on the volume only, the air in the water-separator, though saturated with water vapour as far as its *volume* is concerned, is "dry" from the point of view of its *mass*.

The air now passes into a second vertical cylinder H containing lumps of caustic potash, to remove water vapour and traces of carbon-dioxide, and is delivered pure and dry at the top of the Hampson liquefier. The caustic potash cylinder rarely requires to be refilled, and only after some weeks' working is it necessary to open the valve at the bottom and run off the small quantity of water which accumulates in it.

The Hampson apparatus consists of two or four coils which are wound coaxially about a spindle, and which are joined at their lower ends to a vertical jet: the coils fill the whole space KK. The jet L can be closed by means of a rod which screws down on top of it, and which can be adjusted to form an annular opening by the milled screw-head M outside the apparatus. The coils are enclosed by a cylinder of insulating material for the greater part of their length, but the lower part and the valve are contained in a vacuum vessel N (p. 208), in which the liquid air eventually collects. The liquid is run off through the tap O; the air which escapes liquefaction passes upwards over the outside of the coils and escapes at an opening P at the top of the insulating casing. The escaping air passes through a rubber tube, and its velocity is

indicated by a glycerine gauge which is connected with the point of exit from the apparatus. The doubling of the coil is merely to avoid the risk of blocking the apparatus in case a trace of moisture were carried over from the purifying cylinder; in Linde's apparatus the copper coil is double, the two pipes being concentric, the air passing down the inner pipe and back through the space between the two.

The latest form of the Hampson apparatus is shown in Fig. 101. The air enters under pressure through A, and passes along B to C, where it enters the coil, which is in this case quadruple. On expanding at the valve D it is partially liquefied, the liquid collecting in the metal chamber E, which is soldered directly to the casing of the coil: the gaseous air passes upward through the interstices between the coils, as has already been described.

To indicate the quantity of liquid in the chamber E, a glycerol gauge is employed. The tube K passes from the bottom of E to the top of a small closed

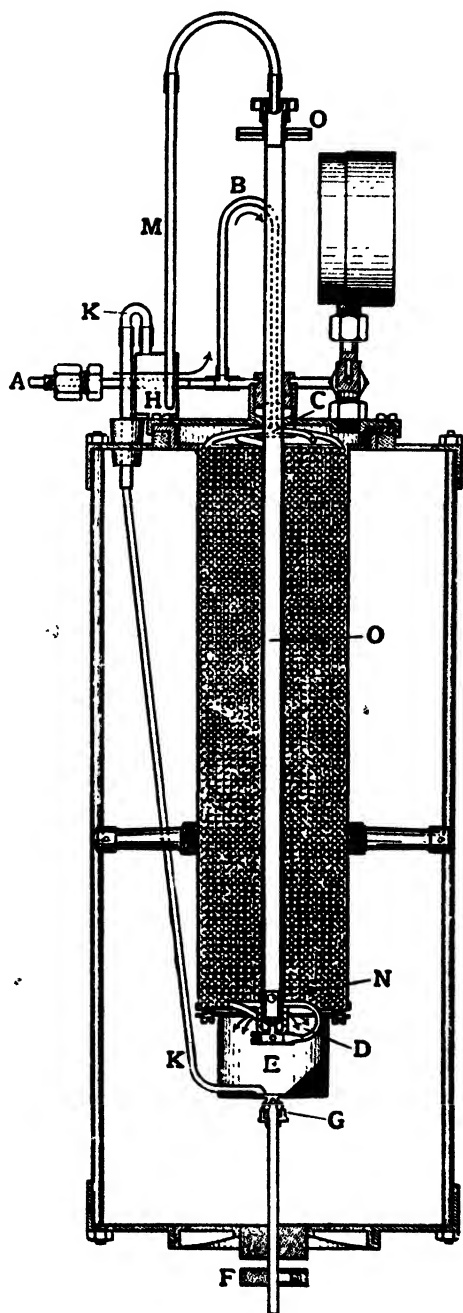


FIG. 101.



vessel H containing glycerol. The vertical tube M, which passes to the bottom of H, is connected by a flexible tube with the top of the valve-rod O, which is hollow, and has an opening at N communicating with the open space above E. As E fills with liquid air, the glycerol rises in the gauge. The liquid air is from time to time run off from E by turning the milled nut F, which opens the screw-down cock G.

In working the apparatus the motor, which is not shown in the figure (Fig. 100), is first started, and a little air is blown through the whole system: the valve is then closed, and the pressure is allowed to rise to 170 atmospheres. When the valve is opened, the stream of air is regulated so that the pressure indicated by the glycerol gauge (p. 192) remains constant. The actual pressure depends upon the length and diameter of the rubber tube R, and upon other conditions: with a tube about 80 cm. long and 2 cm. in diameter it is found to be about 10 cm. of glycerol. Liquid air first appears in the vacuum-vessel in about four minutes, and the actual yield is about 1.15 litres of liquid air per hour.

The machinery requires careful watching while it is at work, for in case anything were suddenly to go wrong a serious accident might result. If every part is working well it is only necessary to draw off the liquid air, and the water which accumulates in the water-cylinder, from time to time; if instead of a vacuum-vessel the liquid air collects in a vessel packed round with some insulating material such as eider-down or animal wool, the liquid air must be drawn off every four or five minutes by the watch. The methods employed in the manipulation of liquid air will be dealt with later.

From the theoretical standpoint the Hampson machine may be regarded as a form of the Joule-Thomson apparatus; for we may consider the plug in the latter as consisting of a number of fine tubes placed close together. The air in passing through the coil does work only against friction, as in the Joule-Thomson experiment, so that there is no cooling owing to external work being done. The air which escapes from the valve has undoubtedly a greatly increased kinetic energy, so that at this point, and at a very small distance from it, the effect due to *velocity-cooling* (p. 190) might be observed: it would, however, be completely nullified owing to the formation of eddy currents long before the gas reached the coils. The form of the jet, and the fact that it is enclosed

in a box containing a helical strip of metal to give the escaping spray a rotatory motion, and to assist in separating the liquid and the gas, would also tend in this direction. The cooling which takes place is thus due to *internal work* only.

The gas which escapes from the valve passes back over the coils, cooling them and the air which they contain; and so perfect is the heat interchange, that the air which leaves the apparatus is only one degree colder than that which enters it. The actual quantity of the air which is liquefied is about 5 per cent of the quantity which passes through the apparatus. It appears probable that no liquefaction actually takes place within the jet, and that the gas at the moment of its escape is not cooled many degrees below its critical point.

With Hampson's apparatus it is possible to liquefy air or oxygen compressed into cylinders at 125 atmospheres. The apparatus is first cooled to  $-80^{\circ}$  C. by blowing a mixture of solid carbon dioxide and air through it. The method would not be used if a compression pump were available.

*The liquefaction of hydrogen.*—The earlier attempts to liquefy hydrogen by the application of pressure alone have already been described, and it is unnecessary to again call attention to the cause of failure. In 1879 Pictet believed that he had accomplished the liquefaction of this gas, which he described as condensing to a steel-blue liquid; but since he obtained his hydrogen by heating potassium formate, it must have consisted largely of carbon monoxide.

In 1883 Wroblewski showed that when hydrogen, compressed into a glass tube cooled to the temperature of liquid oxygen, was allowed to expand from a pressure of 100 to 1 atmospheres it became partially liquefied, the liquid appearing as a mist or spray. In 1885 Olszewski (*Phil. Mag.* [5], xxxix. 199; xl. 202) confirmed these experiments, using first a glass tube of 7 mm. diameter, and afterwards a steel cylinder. The critical pressure of the gas was first determined by measuring the pressure at which mist or spray appeared when the gas compressed into the glass tube and cooled to below  $-200^{\circ}$  C. was allowed to expand: it was found to lie at 20 atmospheres. The boiling and critical temperatures were then determined in the following manner. The steel cylinder already referred to was lined with glass, and contained a coil of platinum wire wound

on a mica or ebonite frame. The resistance of this coil, which communicated with the outside, had been determined at  $0^{\circ}$ ,  $-78^{\circ}$ ,  $-182.5^{\circ}$ , and  $-208^{\circ}$  C. The apparatus was cooled to the temperature of liquid air boiling *in vacuo*. Hydrogen was compressed into the cylinder under a pressure of 170 atmospheres, and the gas was allowed to escape at a cock till the pressure fell to 20, 10, or 1 atmosphere. The resistance of the coil was found in each case by repeated trial, and the temperatures were determined by linear extrapolation. The following results were obtained:—

20 At.	383 Ohms.	$-234.5^{\circ}$ C. (Critical
10 „	369 „	$-239.7^{\circ}$ „
1 „	353 „	$-243.5^{\circ}$ „

That the temperatures obtained by this method are too high is obvious, since the resistance of a platinum wire is not a linear function of the temperature. They serve, however, to show that the critical and boiling points of hydrogen lie below 39 and 29 absolute respectively. Dewar's most recent determinations of these constants are as follows:—

Critical point . . .	$-238$ to $-240^{\circ}$ C.	Critical pressure, 15.3 At.
Boiling point . . .	$-252$ to $-253^{\circ}$ „	
Melting point . . .	$-256$ to $-257^{\circ}$ „	
Lowest temperature obtained by evaporating solid hydrogen $-260^{\circ}$ C.		

As these temperatures were determined by means of the hydrogen thermometer, they may err in the opposite direction, since traces of impurity would separate from the hydrogen as non-volatile solids.

Within the last two years Dewar (*Chem. News*, March 1900) has shown that when hydrogen compressed to 200 atmospheres is cooled to,  $-200^{\circ}$  C. and allowed to expand without doing external work, it behaves similarly to air, or any other imperfect gas, and becomes cooled. He has applied this discovery to the production of liquid hydrogen in quantity; the method of procedure has not, however, been published. The following method by which liquid hydrogen may easily be obtained is described in a paper read before the Physical Society, in November 1900 (Travers, *Phil. Mag.* 1901, 411).

In a preliminary experiment the gas at a pressure of 200 atmospheres was cooled to  $-80^{\circ}$  C. by passing through a coil immersed in a mixture of carbonic acid and alcohol, and was

then allowed to expand at the jet of a Hampson air-liquefier, in which the coil had previously been cooled to the temperature of liquid air. Under these conditions it appeared that progressive cooling did not take place, and it may be concluded that at  $-80^{\circ}\text{C}$ . hydrogen is still a *perfect* gas. The Joule-Thomson effect evidently changes sign at a much lower temperature.

Four attempts were made to liquefy hydrogen before an apparatus was constructed which gave satisfactory results. These experiments I shall not describe; it suffices to state that they served to show that hydrogen remains a perfect gas down to very low temperatures.

The details of the structure of the apparatus finally employed in liquefying hydrogen are shown in Fig. 102. Fig. 103 indicates the general arrangement of compressor, etc.

The principle of the liquefier is briefly as follows. The hydrogen, under a pressure of 200 atmospheres, passes through a coil A, which is cooled to  $-80^{\circ}\text{C}$ . in a mixture of solid carbonic acid and alcohol. It then enters the coil contained in the chamber B, which is continually replenished with liquid air during an experiment. The lower portion of this coil passes into the chamber C, which is closed and communicates through the pipe *ff* with an exhaust pump; liquid air flows continuously from B into C through a pin-valve controlled by a lever *b*, and boiling under a pressure of 100 mm. of mercury, lowers the temperature to below  $-200^{\circ}$ . The gas now passes into the regenerator coil D, which is enclosed in the vacuum-vessel H, and expanding at the valve E passes upwards through the interstices of the coil and the annular space F, surrounding B and C, to the outlet G, whence ~~it~~ can return through the tubes W and R, and the cock *i* to the main supply pipe N. The liquid which separates from the gas is ultimately collected in the vacuum-vessel K, which can easily be removed.

In constructing the apparatus the coil D was wound on the thin steel tube *c*, which contains the valve-rod. The latter is screwed at its lower end into a perforated brass cylinder, soldered to the end of *c*, enclosing the expansion jet. By turning the milled head *a*, the width of the annular space between the jet and the end of the valve-rod could be accurately adjusted, and the flow of gas controlled. This valve was made for me by Brin's Oxygen Company after the pattern of Dr. Hampson, who

first applied it in his apparatus for liquefying air. To the use of this form of valve I must attribute the success of the work, for, unlike the pinhole valve, it does not become blocked with the impurities which separate from hydrogen obtained by treating commercial zinc with sulphuric acid. The coil itself consisted of 80 feet of solid drawn copper tube of  $\frac{5}{16}$  inches internal, and  $\frac{9}{16}$  inch external diameter. In winding it the spiral ran alternately away from and towards the central tube, and great care was taken to preserve a uniform external diameter of  $2\frac{3}{4}$  inches. The tubes were carefully spaced and fixed in position with solder as each layer was wound.

The length of the regenerator coil D is 7 inches, and it must be pointed out here that in absence of all quantitative knowledge as to the behaviour of hydrogen at low temperatures the choice of this dimension, though mainly a matter of guesswork, was arrived at by taking the length of coil in the Hampson liquefier, and reducing it so as to effect a heat interchange of 2° with a difference of temperature of 50° C. between the top and the bottom of the coil.

The next step in the construction of the apparatus was to fix the flanged plates *d* and *e*, which form the top and bottom of the chamber B, on to the tube *c*. The coil passes through both these plates, and *e* is also pierced for the passage of the exhaust pipe *f* and the liquid valve-rod *b*; the latter is screwed through a block fixed to the upper surface of *e*, so that by turning it the conical point closes the hole in the plate to a greater or less extent. All these junctions were made with hard solder; the tube *g*, which fits exactly over *d* and *e*, was then fixed in position with soft solder.

To allow of the escape of the hydrogen gas after its passage through the coils, a brass tube *k* of the same external diameter as the coil is fitted at the top to *g*, by means of a collar soldered to both tubes, and supported by distance pieces at the bottom. The annular space F so formed communicates with the escape pipe G, as shown in the figure and section; the cold gas passing through it forms an excellent insulator for the liquid air chambers B and C.

To support the whole apparatus, and to afford a means of securing the vacuum-vessel H, a collar I is soldered to the tube *k* and to a tube *m*  $3\frac{1}{2}$  inches in diameter, which rests on a flange *n*





in a hole in a shelf attached to the wall of the compressor room. The space between *m* and *h* is packed with animal wool, as is also the space within the containing cylinder *Q*.

The vacuum-vessel *H* is of such a diameter that when the coil *D* and the tube *h* are covered with a single layer of flannel it exactly fits over them. To make gas-tight junction a rubber ring which fills the space between the vacuum-vessel and the inner wall of *m* is pressed between a brass ring *o* and a gland *p*. The ring *o* rests on three short studs on the inside of *m*, and the gland is forced home by three nuts and screws *qq*, which are fixed at their upper ends into the flange *n*.

When the gland is in position the only means by which gas or liquid can escape from the apparatus is by the tube *G*, or through the opening at the bottom of the vacuum-vessel *H*. It is, of course, intended to draw off the liquid at the latter opening, and as it is quite impossible to employ a stopcock for the purpose the following arrangement was adopted. The vacuum-vessels *H* and *K* are both enclosed in a glass tube *LL*, which is closed at the bottom and is connected at the top by a rubber sleeve *s* to a brass tube *h* which forms part of the gland *p*; a short copper tube is soldered into *s*, and terminates in a stopcock *r*. When *r* is closed any liquid formed at the valve *E* is retained in *H*, but when *r* is opened the liquid can flow into *K*, as the gas produced by its evaporation can then escape. The lower part of the tube *L* is enclosed in a large vacuum-vessel *M*, which contains a small quantity of liquid air during the experiment; it serves rather to prevent the frosting of the outside of *L* than to exclude heat.

The hydrogen escaping from *G* passed through the rubber tube *W* into the tube *R*, which communicates directly with the cylinder *P*, and through the stopcock *i* with the main supply pipe *N* connecting the gasometer and the compressor. The cylinder *P* (Fig. 103) is of sheet zinc, and is soldered to the three brass tubes *R*, *S*, and *T*. The tube *S*, which is lined with glass and has a window in front and behind, contains the nozzle of the tube *u* leading from the cylinder *μ*, in which the water used to lubricate the cylinders of the compressor is separated; this arrangement prevents the loss of the gas which escapes each time the water is discharged. The tube *T* reaches to the bottom of a deep vessel (Fig. 103) filled with water; it serves also as an escape for the gas issuing from *G* before the cock *i* is opened.



The tube *f* communicates with an exhaust pump, which is not shown in either figure. It is a simple double-action pump with a single cylinder of 3-inch bore and 6-inch stroke, and driven by a half horse-power gas engine maintains a vacuum of 100 mm. of mercury in the chamber C. The barrel and plug of the stopcock *t* are bored so that C can be cut off from the pump and opened to the air. Through the stopcock *r* the pipe G can be placed in communication with the exhaust pump.

It is now convenient to call attention to the general system of heat insulation in the apparatus. The coil A is surrounded

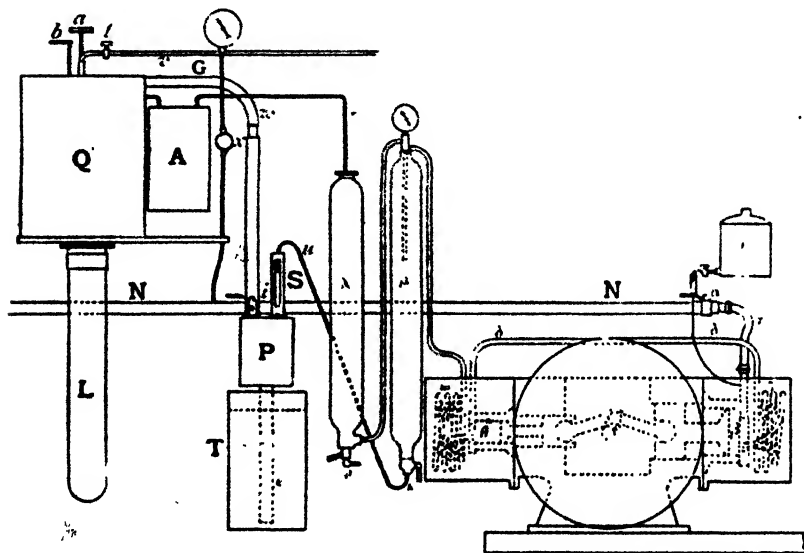


FIG. 103.

with solid carbonic acid and alcohol contained in an earthenware battery jar, which is unprotected. The tube between A and B is surrounded with a wrapping of animal wool and covered with baize. B and C are protected by the cold gas which returns through the annular space F after passing through the regenerator coil D; additional protection is afforded by the layer of animal wool inside the cylinder Q. The increasing steepness of the temperature gradient at C is compensated for by the protective influence of the upper part of the vacuum-vessel H, while the vacuum-vessel M, which contains liquid air, serves as a protection to K and to the lower part of the regenerator coil D. It also prevents deposition of moisture on the tube L. The method of

supporting the apparatus by the tube  $m$  answers admirably, for as the space between  $m$  and  $k$  is packed with wool, the gland  $p$  only becomes frosted over when the experiment is at an end, showing that the influx of heat in this direction is inconsiderable.

The hydrogen gas is obtained by the action of dilute sulphuric acid on commercial granulated zinc, and was stored in a gasometer over water. The gasometer consists of a cylinder of sheet-iron (No. 16 gauge) 6 feet in height, and 5 feet 6 inches in diameter, inverted in a cylindrical tank, which is filled with water. The gas enters and escapes through a 2-inch iron pipe passing through the bottom of the tank, and terminating inside a small dome 6 inches in diameter on top of the inner cylinder. This arrangement makes it possible to expel the whole of the gas from the gasometer without danger of introducing water into the supply pipe. Before filling the gasometer the water in the tank is saturated with hydrogen by passing a stream of the gas through a tube reaching to the bottom. This operation occupies about five days, but it is not necessary to repeat it.

The main bulk of the hydrogen is generated in the following manner:—About 40 lbs. of zinc are placed in a beer-cask fitted with a tap funnel, a delivery tube, and an escape pipe, which passes into a vessel filled with water, and so acts as a safety valve; a stoneware cock at the bottom for drawing off spent acid. When all the air has been expelled from the cask the gas, after passing through a wash-bottle filled with a solution of potassium permanganate, is allowed to enter the gasometer. The latter is thoroughly *washed out* with hydrogen before the main quantity is collected. The preparation of the hydrogen occupies five hours.

The general arrangement of the plant for the compression of the hydrogen, which passes through the pipe  $NN$ , the cock  $a$ , and a temporary communication made by means of a lead pipe  $\sigma$ , with two screw unions, is shown in Fig. 102. The hydrogen, or air when the latter is to be liquefied, is first of all taken into the low-pressure cylinder  $\beta$  of the compressor, which has already been described on p. 190, and, passing thence through the coil, kept cool by a current of water which circulates through the tanks surrounding the cylinders and coils, enters the high-pressure cylinder  $\theta$  through the tube  $\delta$ , under a pressure of about 16 atmospheres. A small quantity of a mixture of

glycerol and water containing 5 per cent of caustic soda is taken into the low-pressure cylinder, together with the gas. The mixture is contained in the vessel  $\eta$ , and the flow is controlled by the glass stopcock and the arrangement shown in Fig. 103. In the second cylinder the pressure is raised to about 200 atmospheres; and the gas, after passing through the coil  $\omega$ , enters the cylinder  $\mu$ , in which the water used in lubricating the cylinders is separated and expelled through the cock K. This water, together with a little gas, passes along the tube  $\nu$ , and enters the cylinder P; the water flows into the tank  $\epsilon$ , and during the compression of the hydrogen the gas is allowed to return to the gasometer through the cock  $i$ . The details of this part of the apparatus have already been described.

The gas from  $\mu$  passes into the cylinder  $\lambda$ , which contains lumps of solid caustic potash to remove traces of moisture or of other impurities. This cylinder is employed in compressing both air and hydrogen, and can be connected by the tube  $\tau$  either with a Hampson air-liquefier, or, as in the figure, with the coil A of the liquid hydrogen apparatus. The tube  $\tau$  also communicates with a gauge, and with a cock  $x$  through which, if the pressure becomes too high, the excess of gas may be allowed to escape into the pipe XX connecting the gasometer and the compressor. The liquefier, of which the detail has already been given, does not require further description. It is sufficient to state that the gas, after passing through the coils in Q and L, expands at the valve  $s$ , controlled by the milled nut  $a$ , and finally returns by the tubes G, W, and R, and the stopcock  $i$ , to the tube N.

The loss of gas during each experiment amounts to about 10 per cent of the whole; and since air and other gases of higher boiling point separate as solids in the vacuum-vessel H, the gas becomes purer each time it is used.

During the two or three days immediately preceding an experiment the compressor is employed in producing liquid air, as described on p. 190. The liquid air is stored in vacuum-vessels holding altogether about 8 litres. Comparatively little loss occurs through evaporation, and the vessels are usually filled up on the last morning. After preparing the liquid air it is advisable to take the compressor in pieces and carefully inspect the valves, springs, and fibre-packings. In the meantime the Hampson machine is removed, the connections are made between the potash

cylinder and the hydrogen liquefier, and the lead pipe  $\sigma$  connecting the supply pipe NN with the intake of the compressor is placed in position.

The actual experiment requires four persons: one controls the valves  $a$  and  $b$ ; the second attends to the compressor, regulates the escape of the water from the cylinder  $\mu$ , and opens or closes the cock  $x$  as the pressure rises or falls; the third sees that the vessel in which the coil A is immersed contains sufficient solid carbon dioxide; the fourth hands the vacuum-vessels of liquid air as they are required.

The first step in the operation is to cool the liquefier to the temperature of liquid air. Liquid air is first poured into the chamber B, and is allowed to flow into C by connecting it with the exhaust pump through the cock  $t$ , and turning the valve  $b$ . When C is partially filled, and the vacuum gauge indicates that the liquid air is not evaporating at a great rate, the valve  $b$  is closed, and the cock  $t$  is turned so as to cut off the exhaust and leave the chamber C open to the atmosphere (p. 200).

The vacuum-vessel M, and the tube L with the vacuum-vessel it contains, are moved by rolling up the rubber sleeve  $s$  into the tube  $h$ , and lowering the cradle in which M is suspended. The rubber cap carrying the cock V is then fitted to the nozzle of H, and connected with a rubber tube dipping into a vacuum-vessel filled with liquid air.

The escape-pipe G, from which the rubber tube has already been removed and replaced by a rubber cork, is now connected with the exhaust pump through the cock  $v$ . Liquid air is drawn into the vacuum-vessel H, and on closing the cock  $v$  boils under reduced pressure, cooling the regenerator coil to below  $-200^{\circ}$  C. By closing the cock  $v$ , removing the rubber cork, and opening the stopcock  $r$ , the liquid flows out of H. The rubber cap securing  $v$  is now moved, the tube L and the vacuum-vessels M and K are replaced in position, and the rubber sleeve  $s$  is secured to L with a single turn of copper wire.

Meanwhile the assistant in charge of the compressor has removed all air from the compression apparatus by opening the cock  $a$  (Fig. 103), allowing the compressor to make a few revolutions, and then stopping it and opening the cock  $p$ . This operation is repeated three or four times: the pressure is then allowed to rise, the valve  $a$  (Fig. 102) being closed, and the gas is allowed

to escape, if necessary, through the cock *x* into the pipe N. The arrangements are made so that the pressure is raised to 200 atmospheres by the time the liquefier has been cooled and the vacuum-vessels K, etc., replaced in position.

The remaining operations may be shortly described. Communication is once more established between the chamber C and the exhaust pump, and the valve *b* is carefully regulated, so that the liquid air does not enter too fast: too rapid a flow is at once indicated by a fall of the mercury in the vacuum gauge. The expansion valve is then opened by turning the milled nut *a*, and the gas passing upwards through the coils, through the annular space F, and through the tubes G, W, and R, finds its way into P, and, in order to remove air from the apparatus, is allowed for a few moments to escape through the water in the tank *e*. The cock *i* is then opened, and the gas is allowed to circulate through the system. The chamber B and the vessel containing the coil A are continually replenished with liquid air and with solid carbonic acid respectively.

The whole difficulty in this part of the experiment lies in properly regulating the escape of the hydrogen. The rate of flow of the gas is roughly indicated by the height of the glycerol in the gauge *z*, which shows the pressure in the interior of the apparatus caused by the friction of the gas in the tubes G, W, and R. It is intended in future experiments to introduce, in place of W, a coil of lead pipe, and to connect the top of the glycerol gauge with a tube leading into the cylinder P, as it will then give an absolute reading of the rate of flow of the gas.

The reasons for which it is necessary to carefully regulate the valve are twofold. Firstly, the hydrogen must not pass too quickly through the refrigerating coils, or the gas is insufficiently cooled: secondly, since liquid hydrogen has a very low and specific gravity (0.06) the gas and liquid do not separate easily at the jet, and much of the latter is lost. Further, since the efficiency of the regenerator coil is dependent on the rate of transmission of heat through its walls, and this is proportional to their superficial area, the maxim effect is attained with a limited quantity of gas.

To guard against blocking of the valve by the deposition of solid impurities, the milled nut *a* is turned slowly backwards and forwards during the whole experiment. The screw at the end

of the valve-rod fits so tightly into the brass cylinder containing the jet that no gas can escape from the liquefier through the steel tube *c*, and it is necessary at times to apply some force to *a*. In constructing another machine I should either place the screw on the valve-rod in the tube *c*, about 2 inches above the valve, or I should ease the screw in its socket and place a gland round the valve-rod at the top of steel tube *C*.

There appears to be no danger of the coil becoming blocked through the deposition of solid matter inside it, even though the hydrogen contains 2 or 3 per cent of air and perhaps traces of arsenuretted hydrogen, hydrocarbons, etc. It must be remembered that within the regenerator coil, even very close to the jet, the temperature of the gas does not fall below its critical point, or it would become filled with liquid, and it appears that this is not the case. Under these conditions a gas is capable of holding a considerable quantity of solid matter *in solution*, a phenomenon which has not been fully explained. This may account for the fact mentioned above. Solid impurities do, however, separate from the liquid in the vacuum-vessel *H*; but as the liquid on its way to the vessel *K* is obliged to pass through a piece of baize pressed down into the bottom of *H* by a spring, it can be collected as a perfectly clear liquid.

Almost immediately the valve *E* is opened the inside of the vacuum-vessel *H* becomes coated with a layer of white matter, which is probably solid air. The cock *r* is from time to time turned, and shortly, by placing a light behind the lower part of the apparatus, liquid is seen running in a fairly rapid stream from the nozzle of *H*, and collecting in *K*, which rapidly becomes filled. The flow of the gas from the jet can then be checked, the tubes *M* and *L* lowered, and the vacuum-vessel *K*, which is attached to a wire, withdrawn and placed in another vessel containing a little liquid air. It would then be possible to replace another vacuum-vessel in *L*, to restore *L* and *M* to their original positions, and to prepare a further quantity of liquid hydrogen. This has not, however, been attempted.

• The apparatus which I have described, with the exception of the compressor, the motor, and the Hampson air-liquefier, which together cost about £200, is comparatively inexpensive. The gasometer cost about £15, the material used in making the liquefier amounted to about £5; and possibly, in addition to the sum

named, another £30 was spent in the experiments. Each time liquid hydrogen is made, 5 kilos. of solid carbonic acid and 8 litres of liquid air are used. This involves a further cost of about £1. These figures indicate that the cost of liquid hydrogen is not excessive.

NOTE.—Since this account of the method of liquefying hydrogen was written, the apparatus has been somewhat altered. It was found that the dimensions of the coil B were insufficient to cool the gas rapidly to the temperature of liquid air. This difficulty was overcome by inserting a coil, similar to A, between A and B, and surrounding it with liquid air.

## CHAPTER XVI

### THE MANIPULATION OF LIQUEFIED GASES

Vacuum-vessels—Condensation of gases—Constant temperatures by means of liquefied gases—Fractionation of liquefied gases—Distillation of atmospheric nitrogen—Separation of the inactive gases—The composition and boiling point of liquid air—Fractional distillation of a mixture.

**THE MANIPULATION OF LIQUEFIED GASES.**—The introduction of the now well-known vacuum-vessels by Dewar has rendered the manipulation of liquefied gases a matter of comparative simplicity; and as these vessels in one form or another are extensively used in this kind of work, it will be well to say something about their construction and use.

The usual forms of vacuum-vessels are shown in Fig. 104. They may be either cylindrical or globular, and their size is limited only by the diameter of the mouth where the junction between the inner and outer tube is made. It may be noted that the vessels are less liable to crack at the junction if the junction between the two glass tubes lies on the outside.

The space between the glass walls must be very thoroughly exhausted. A Töpler pump (p. 7) may be used for the purpose, and the exhaustion should be continued until a vacuum tube attached to the apparatus shows a brilliant phosphorescence under the influence of the electric discharge (p. 301). The tube should be heated

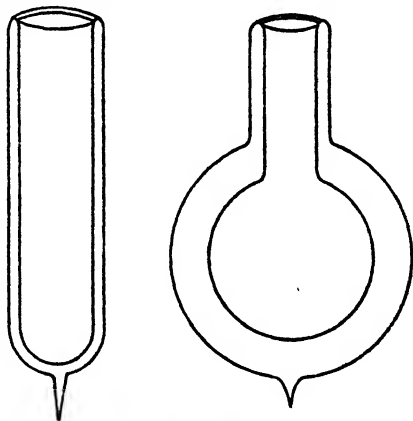


FIG. 104.



during the exhaustion. Onnes employs an asbestos oven heated by coils of wire, through which an electric current is passed. The tube is heated both on the inside and on the outside.

The evaporation of liquid air contained in a good vacuum-vessel takes place only very slowly, since the heat radiated across the vacuous space is only one-seventh of the total heat which would reach the inner vessel were the jacket to contain air. The efficiency of the vessel may be still further increased by introducing a globule of mercury into the vacuous space; the mercury vapour deposits in a metallic layer on the surface of the inner vessel, partially reflecting radiation from the outside. The tubes may be silvered on the inside by one of the usual chemical processes. Hempel *Ber.* 1898, **31**, 2933 states that a layer of eider-down is a more efficient insulator than the vacuous space; it is, however, usually necessary to observe what is taking place inside the vessel. The addition of a layer of insulating material is at the same time an advantage if the liquid air is to be preserved for a long time, three or four hours or more, or transported from place to place.

Liquid air may be poured from one vessel to another without danger of cracking the glass, if a little of the cold vapour is allowed to flow over the edge of the first vessel into the second before the liquid is poured out. If the vessels are made so that the joint between the inner and outer cylinder lies on the outside of the lip, which is carefully rounded, they are much less liable to crack than if the junction is made so that the liquid can come into contact with it when it is poured from the vessel. If, however, the glass does crack, the vessel usually flies to pieces with a loud report, but without doing damage. The liquid may be transferred from one vessel to another by introducing into it a syphon passing through a rubber stopper which fits into the mouth of the vessel. The stopper should be held down by hand so that the pressure of the vapour forces the liquid through the syphon. The syphon should be made of rubber tube of 5 mm. diameter.

Vacuum-vessels for use with the Hampson liquefaction apparatus and for similar purposes are made with an opening at the bottom (Fig. 2); the spiral connecting tube gives sufficient elasticity to eliminate strain. The liquid air may be drawn off through a metal tap connected by a rubber junction with the

projecting glass tube. The tap should always be opened very slowly so as to allow the cold vapour to pass through the spiral before the liquid enters it. It is usually necessary to close the top of the vessel with the hand so as to force the liquid through the tap.

It must not be forgotten that the temperature of liquid air rises rapidly as the nitrogen evaporates, and that its boiling-point cannot be taken as definite, as has been assumed by some observers. The temperature can always be determined by means of a hydrogen or platinum resistance thermometer, or by making an analysis of the vapour which is being given off by it (p. 224). Constant temperatures can only be obtained by means of pure liquids; and by employing methyl chloride, sulphur dioxide, nitrous or nitric oxides, ethylene, methane, oxygen, nitrogen or carbon monoxide, boiling under different pressures, an almost complete range of temperature down to  $-210^{\circ}\text{C}$ . can be arrived at.

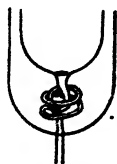


FIG. 105.

A gas may be condensed in a glass tube surrounding the bulb or other apparatus to be cooled, as in Fig. 111, p. 228, or it may be liquefied in a tube and the liquid delivered by a syphon into a vacuum-vessel for the experiment. In either case all the connections must be air-tight so as to avoid loss of the gas, which becomes purer from the repeated fractionation to which it is subjected. The gas should be freed from water or alcohol vapour, or the liquid will be opaque; and arrangements should be made to pump off any uncondensable gas which may be present, and which would collect on the condensation bulb. The tube in which the gas is condensed is surrounded with liquid air in a vacuum-vessel. If, as in the case of ethylene, the liquid solidifies, it is necessary to lower the vacuum-vessel to allow the solid to melt and to run to the bottom of the tube. On the other hand, it will only be possible to liquefy nitrogen or carbon monoxide either by the application of pressure on the gas or by making the liquid air in the surrounding vessel boil under reduced pressure (p. 210). If the liquid is to be allowed to boil in the tube in which it is condensed, as soon as a sufficient quantity has collected, the vacuum-vessel should be lowered so that the condensation tube is quite free of the liquid air: the mouth of the vacuum-vessel is then plugged with wool. By this means the condensed gas only receives heat slowly, and when its temperature rises to the

boiling-point evaporates quickly. Further, no moisture is deposited on the outside of the tube, and this is often highly important.

The determination of the boiling-point of liquefied gases will be dealt with in Chapter xvii., and it is only necessary to state here that it is sometimes essential to guard against superheating of the liquid. This may easily be done by passing a stream of the gas through a fine capillary tube through the liquid (p. 213), or by dropping small scraps of metal into it. This is particularly important in the case of nitrogen, of freshly-made liquid air, or of liquid air boiling under reduced pressure. In the latter case Estreicher employed a current of hydrogen (p. 239).

It is extremely difficult to maintain a constant temperature by evaporating a liquid under very low pressure. A small reduction of pressure may be obtained by connecting the vessel containing the liquid with a water-pump; a gauge and a large globe should be interposed (p. 316). Very low pressures can only be arrived at by means of a mechanical pump; and if one considers that 1 c.c. of liquid air evaporating under a pressure of 8 mm. of mercury gives rise to 100 litres of gas, this is hardly surprising. At the same time a very considerable lowering of the temperature can be effected for the purpose of separating gases by fractional distillation by the use of a Fleuss or Carré pump. A considerable advantage is obtained by surrounding the vacuum-vessel containing the liquid air boiling *in vacuo* with another vessel also containing liquid air.

*The separation of the gases in a mixture by fractional distillation.*—As a method for the preparation of pure gases this process was first employed by Olszewski in the case of ethylene and afterwards by Kuenen to the preparation of pure ethane, by Dewar to the separation of helium from Bath gas, and by Ramsay and Travers to the separation of the inactive gases of atmospheric air. The method is capable of wide extension, and is at present the only one by which hydrogen or nitrogen may be separated from gases, such as the hydrocarbons or oxides of nitrogen; the applications of liquid air in this direction have yet to be worked out. Since all known gases (with the exception of hydrogen, neon, and helium) can easily be liquefied at a pressure of a little over one atmosphere at the temperature of liquid air,

the operation can be carried out in thin-walled glass vessels. To illustrate the method of operation it will be well to describe a few of the experiments which have actually been carried out.

1. *Separation of ethylene from gases of lower boiling-points.*—The action of sulphuric acid on ethyl alcohol gives rise to the formation not only of ethylene but also of considerable quantities of carbon dioxide, sulphur dioxide, and carbon monoxide. The first two may easily be absorbed by caustic soda; the ethylene may very easily be condensed and solidified at the temperature of liquid air, its boiling-point being  $-102.5^{\circ}$ ; the carbon monoxide, however, boils at  $-191^{\circ}$ , and can only be condensed by the application of pressure. The apparatus employed is shown in Fig. 106.

The U-tube *a*, which contains a strong solution of caustic soda, is connected with the gasholder containing the mixture of gases, and with a tube *b*, which passes through a rubber stopper in the neck of the liquefaction bulb and reaches nearly to the bottom. The tube *b* should be about 15 mm. in diameter, or it may become choked with solid ethylene. The tube *d* is connected through a two-way stopcock *c* with a gasholder to receive the pure ethylene, and with a tube *f* which dips below the surface of the water or mercury in a vessel.

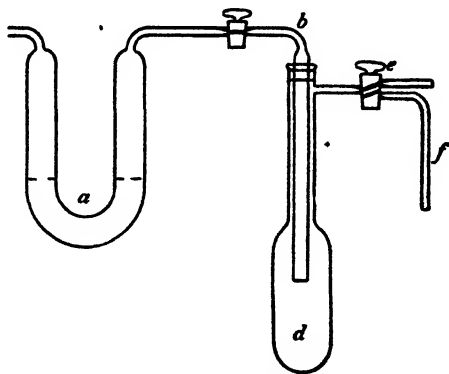


FIG. 106.

The apparatus is first exhausted and filled with ethylene, and a vacuum-vessel filled with liquid air is brought below the bulb and raised so as slowly to increase the cooled surface of the bulb. The gas condenses rapidly at first, but after a short time the bulb becomes filled with uncondensable gas and condensation ceases. The stopcock *c* can then be turned so that a slow stream of gas escapes at *f* bubbling through the liquid. The rate of flow of the gas can easily be regulated, so that practically the whole of the ethylene is condensed, while the carbon monoxide escapes. It may, however, be necessary to lower the vacuum-

vessel once or twice during the experiment, as the layer of solid ethylene in *d* is highly non-conducting, and must be allowed to melt so as to leave as large a condensing surface as possible.

When the whole of the gas is condensed the liquid air may be removed, and the first part of the gas, which contains carbon monoxide, allowed to evaporate and pass back through the U-tube into the original gasholder. The remainder may then be collected in the gasholder intended to receive the pure ethylene. To make quite certain that the gas which is being collected is pure, a platinum resistance thermometer may be enclosed in the liquefaction bulb, and the temperature determined during the operation as in the fractional distillation of any other liquid. This is more important in preparing ethane or the higher hydrocarbons.

This method may be employed in the preparation of methane, nitric oxide, and other gases.

2. *The fractionation of atmospheric nitrogen* (*Phil. Trans.* 1901).—In order to obtain the lighter constituents of atmospheric air a quantity of nitrogen, about 100 litres, was condensed in a glass bulb immersed in liquid air boiling under reduced pressure. The gas condensed rapidly under a pressure of about 2.5 atmospheres, and when the bulb was about two-thirds full it was placed in communication with a gasholder, and about five litres of gas was collected.

This gas should have contained the greater part of the neon and helium from a litre of argon, but the actual result was disappointing, for on removing the nitrogen from the gas the inactive residue was found to consist of normal argon only. It appeared that the evaporation of the liquid in the bulb had taken place at the surface only, and that there had been no fractionation. This is probably connected with the fact that liquid nitrogen shows a remarkable tendency to become superheated, and can only be made to boil steadily by passing a current of gas through it.

Since for this reason it was evidently impossible to obtain the helium and neon from air by simple fractional distillation, the following process was successfully employed. It has been pointed out (p. 192) that when the Hampson liquid air plant is so arranged that the air flows in a closed circuit, the quantity of the lighter gases in the unliquefied portion of the

air' continues to increase. Considerable advantage could be obtained by submitting this air to fractional distillation, a process which was carried out in the following manner :—

The blow-off cock *S* on the Hampson machine (p. 191, Fig. 100) was connected with the tube *a* of the liquefaction bulb (Fig. 107), which had a capacity of 120 c.c., and with a mercury manometer about two metres in height. The tube *a* was sealed to a capillary tube which reached nearly to the bottom of the bulb, which was also in communication through a side-tube and a pair of brass stop-cocks soldered to a T-piece with the tube *a*, and with the gasholder in which the lightest fraction of the gas could be collected. The apparatus was immersed as far as the side-tube in a vacuum-vessel containing liquid air.

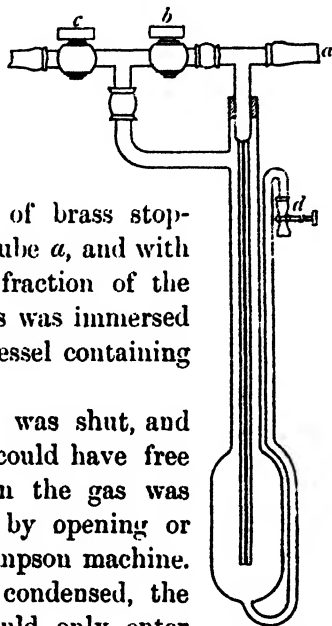


FIG. 107.

During the liquefaction the cock *c* was shut, and the cock *b* was open so that the gas could have free access to the bulb. The pressure on the gas was regulated to about 2.5 atmospheres by opening or closing the escape-cock *P* on the Hampson machine. When about 100 c.c. of liquid had condensed, the cock *b* was closed, so that the air could only enter the bulb through the capillary tube. The cock *c* was then slightly opened so as to allow some of the gas produced by the evaporation of the liquid to pass into the gasholder; as the liquid was thoroughly stirred by the current of gas which entered through the capillary tube, the liquid boiled and did not evaporate from the surface only. When about five litres of gas had been collected, the cock *c* was again closed, and by opening the pinch-cock *d*, the liquid remaining in the bulb was run into the vacuum-vessel surrounding it. After closing *d* the apparatus was ready for a second operation.

In this process the air was found to have undergone an efficient fractionation, for after removing the oxygen and nitrogen from the gas the residue contained at least 10 per cent of a mixture of neon and helium.

3. *The fractionation of atmospheric argon, and the preparation of neon* (Ramsay and Travers, *Proc. Roy. Soc.* **63**, 438; **64**, 183;

*Phil. Trans.* 1901).—The preparation of a large quantity of argon (15 litres), for the purpose of determining whether it would be possible to separate it into its possible constituents by fractional distillation, has already been referred to (p. 106); it remains to describe the method by which the process was carried out, and the results to which it led.

The argon, which was stored over water in a zinc gasometer, was liquefied in the bulb *b* of the apparatus shown in Fig. 108,

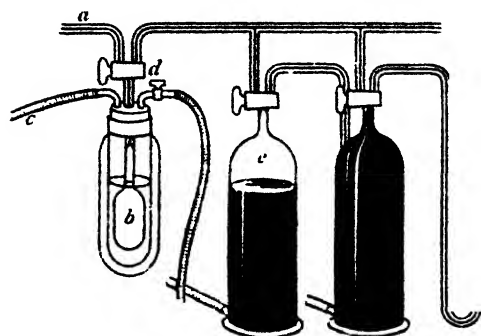


FIG. 108.

which it entered through the tube *a*. The bulb had a capacity of about 25 c.c., and was surrounded by liquid air contained in a vacuum-vessel. The air was made to boil under a pressure of a few centimetres of mercury by means of a Fleuss pump attached to the tube *c*.

The argon rapidly and completely liquefied to a colourless mobile liquid; it showed no absorption spectrum. Its volume was about 17.4 c.c. By turning the tap *d* it was placed in communication with the first of the series of mercury gasholders, *c*; the reservoir was then lowered so as to remove the lower-boiling portions of the liquid. During this distillation, which took place at constant temperature, the pressure on the boiling air was kept as low as possible. This gas subsequently turned out to be rich in neon, and to contain helium. The remainder of the argon boiled back into the gasometer until the last few drops were left; the residue solidified, and finally gave a gas to which we gave the name metargon; it was collected in mercury gasholders. As will be subsequently shown, the krypton and xenon in this quantity of argon are too minute for detection. A similar operation for the purpose of separating the lighter as well as the heavier constituents was afterwards repeated three times, the middle portion of argon being always returned to the large gasholder. A fourth liquefaction was carried out in which six mercury gasholders were filled with six separate fractions of argon, each taken after each successive fifth of the total argon had evaporated. These fractions were next

purified from any nitrogen accidentally present by sparking with oxygen over caustic potash. After the removal of the oxygen the density was determined. The results are expressed in terms of  $\rho = 16$ .

Capacity of Bulb.	Temp.	Pressure.	Weight.	Density.
	c.c.	mm.	gram.	
(1) 37.762	19.05	535.1	0.03786	19.85
(2) „	15.70	712.0	0.05265	19.95
(3) „	17.00	662.2	0.05012	19.95
(4) „	11.55	719.8	0.05460	19.91
(5) „	15.60	740.4	0.05389	19.97
(6) „	16.15	760.2	0.05501	19.95

Fraction 4 certainly contained a trace of nitrogen, and it is probable that fraction 1 still contained some neon, though this could not be detected. The results show conclusively that the inactive constituent of atmospheric air consists almost entirely of argon, and that substance is homogeneous in its character. The density of argon, when more accurately determined, was found to be 19.955.

The light gas obtained by the fractionation of the argon was then submitted to a further fractionation in the apparatus shown in Fig. 109, which has since been frequently employed for similar purposes. The gasholder A is connected, through the stopcock B, with the liquefaction bulb C, which communicates with the Töpler pump through the stopcock D. The gasholder is connected by a rubber tube with a mercury reservoir, and the bulb *c* is surrounded with

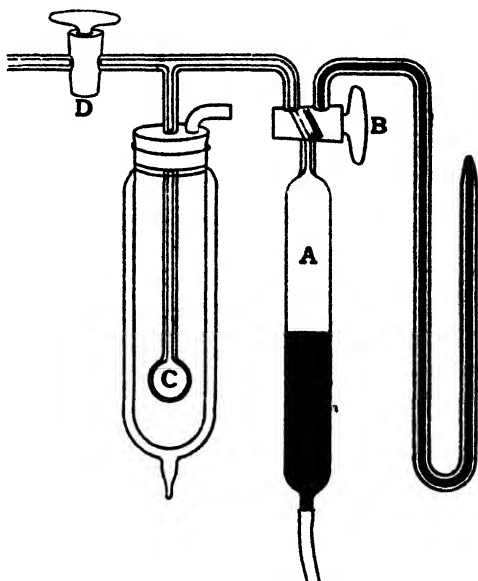


FIG. 109.

liquid air contained in a vacuum-vessel. Before introducing the gas the bulb *c* was exhausted, and to remove air from the bore of



the stopcock the mercury reservoir was lowered so as to produce a barometric vacuum in A, and the stopcock B was turned, as in the figure.

The vacuum-vessel surrounding the bulb C was filled with liquid air, which was made to boil under reduced pressure by means of a Fleuss pump which was connected with it. By immersing the vacuum-vessel surrounding the bulb in another vessel containing liquid air, it was possible to reduce the temperature to  $-205^{\circ}\text{C}$ . without much labour.

The mixture of argon with the lighter gases (1), which had the density 14, condensed without difficulty, and by simply raising the mercury reservoir the whole of it liquefied in the bulb. It was then allowed to evaporate in five approximately equal fractions (2 to 6), in which, as their densities show, the quantity of argon present successively increased. In the following scheme of fractionation the numbers in brackets represent the densities of corresponding fractions---

		16			
		17	- 22	28	
		18		20	20
	-13	19	- 23	31	34 (8.3)
	7 (9.75) -14	20		32	35 (9.8)
2 (13.4)	8 ... -15	21	24 (10.6)	-33	
-3 (16.2)	- 9 (16.5)		- 25		
1 (14.0) -4 (16.6)	-10				Ne and Ar.
-5 (17.2)	-11 (17.7)		26		
-6 ... -	-12 ...		27		

The heaviest fraction (6) was next introduced into the gas-holder, and liquefied. A portion of it, about a quarter, was then allowed to evaporate, and the denser portion which remained behind was removed through the pump and collected separately (12). The lighter gas was then liquefied together with fraction 5, the denser portion forming fraction 11, the lighter portion being mixed with fraction 4 and reliquefied. This process was repeated with each of the existing fractions, with the result that six new fractions of gas were obtained and, as the densities show, a considerable separation was effected.

The lightest fraction, No. 7, which no longer showed the spectrum of argon, had the density 9.7, and could not be condensed at the temperature of liquid air boiling under reduced pressure, even under two atmospheres pressure. In order to fractionate it further, it was mixed with a considerable volume of oxygen, and the mixture was liquefied and allowed to evaporate in three fractions (13, 14, 15). It is noteworthy that while the presence of a small quantity, an equal volume, of argon is sufficient to cause the neon to liquefy, the gas cannot be easily condensed with thirty times its volume of oxygen and nitrogen.

After removing the oxygen from each fraction separately, it was found that in the third (15) alone could the spectrum of argon be detected by visual examination; the other fractions appeared to consist of pure neon. When, however, the spectrum of the lightest fraction (13) was photographed, the helium lines ( $\lambda = 5875$  and  $5016$ ) appeared on the plate. This observation introduced a new feature into the work, for although no difficulty had been experienced in separating the argon from the lighter gas, it appeared probable that the separation of neon and helium from one another would prove considerably more troublesome.

In the next stage of the operations, fractions 13 and 14 were liquefied separately with excess of oxygen, and each was divided into three parts (16, 17, 18,—19, 20, 21). After removing the oxygen and examining the fractions spectroscopically, fractions 16, 17, and 19, which contained the greatest quantity of helium, were combined, as were fractions 18 and 20, which should have contained the purest neon. The two latter, mixed, had the density 8.3; they probably still contained helium in considerable quantity. Fractions 8 to 12, 15, and 21 were further fractionated, and yielded about 20 c.c. of a gas of density 10.6 (24).

Fraction 22 was now divided into two parts (28 and 29) by fractionation with oxygen, and the heavier fraction (29), mixed with fractions 23 and 24, was liquefied with oxygen and divided into four parts. The lightest part (30), as certainly containing helium, was mixed with fraction 28; the two middle fractions were mixed and refractionated with oxygen, the resulting fractions, 34, and 35, having densities 8.3 and 9.8 respectively; the heaviest fraction, a single bubble of gas, consisted almost entirely of argon.

So far, it is probable that the composition of fraction 35 approached most closely to pure neon. It certainly, however, contained both helium and argon, and it was evident that in order to obtain a weighable quantity of the gas, it would be necessary to start from a much larger quantity of the crude material.

The exact details of the various attempts which were made to liquefy neon have been described in a paper before the Royal Society (*Phil. Trans.* 1901). It suffices to state here that though it was found possible to separate the greater part of the argon from the gas by fractional solution in oxygen, there appeared to be no great difference between the solubilities of helium and neon in the liquid.

The separation of these two gases was ultimately accomplished by liquefying them in a bulb cooled by liquid hydrogen. At this temperature the neon condensed, possibly to a solid, and its vapour pressure was not more than 50 mm.; the helium appeared to remain gaseous, while the argon was non-volatile. After condensing the gas the first fraction was taken into the pump (p. 215); it contained a large quantity of helium. The second fraction, which evaporated slowly, was collected separately, and after removing the vacuum-vessel containing the hydrogen, a third fraction containing argon was collected. The second fraction was then recondensed, a small quantity of it was allowed to evaporate into the pump, and the main bulk of the gas was collected as pure neon; the last traces of the gas were again discarded since they might contain traces of argon.

The fraction of the gas supposed to be pure neon was found to have the density 10.

2. *The separation of krypton and xenon from air.*—When liquid air is allowed to evaporate quietly in a vacuum-vessel, the last traces of liquid consist almost entirely of oxygen (p. 223), with small quantities of nitrogen, argon, krypton, and xenon. The latter are present only as traces, as they are present in the atmosphere to so small an extent that they cannot be detected in the residue obtained by the fractionation of 15 litres of atmospheric argon. The Hampson process for the production of liquid air is itself one of fractionation, about 5 per cent of the total air which passes through the coils becoming liquid, and it is probable that the whole of the xenon and part of the krypton are condensed; it is certain that when the air is

made to circulate through the apparatus (p. 191), the quantity of the heavier gases in the residue from the liquid air is very much reduced. Under the most favourable conditions a litre of liquid air might yield 0.1 to 0.2 c.c. of xenon, which may be present in the atmosphere to the extent of 1 part in twenty millions.

The liquid was allowed to evaporate, the gas being collected in a gasholder: the oxygen was removed by passing the gas together with hydrogen through a heated iron tube, and the nitrogen was absorbed by means of the mixture of magnesium and lime. The residual gas was then sparked with oxygen, or passed over heated copper oxide to remove traces of carbon monoxide or hydrogen, and after treatment with soda solution was ready for fractionation.

The first quantity of the gas obtained in this manner (Ramsay and Travers, *Proc. Roy. Soc.* **63**, 405) had the density 22.5, and its spectrum showed the brilliant yellow line,  $D_4(\lambda = 5871)$ . After the first fractionation the fraction, which was supposed to contain the heavier gas, was found to have a density barely exceeding that of argon, though the brilliance of the yellow line was not diminished. It was afterwards shown that the fall in density was due to the complete removal of the xenon, which had remained in the fractionation bulb, as its vapour pressure at the temperature of liquid air is infinitesimal. That the gas of density 20 showed the krypton line brilliantly, though the density of the latter gas is 40.8, is due to the fact that the spectrum of krypton, like that of mercury, is apparent when only a trace of it is present in another gas.

The apparatus employed in fractionating the gas was the same as that employed in separating neon from its companions (Fig. 108, p. 215). When a sufficient quantity of the inactive gases from liquid air residues had been collected, it was liquefied at the temperature of liquid air; the first portion, consisting mainly of argon, was allowed to evaporate into the gasholder A, and the remaining gas, which was rich in the heavier constituents, was collected separately. The last traces of gas were taken off through the pump, the vessel containing the liquid air being lowered to allow the xenon to volatilise completely. In this way about 300 c.c. of heavy gas were obtained.

The whole of this gas (1) was introduced into the gasholder, and after being liquefied was allowed to evaporate in six equal portions (2-7), the last fraction (7) being taken off through the pump after removing the liquid air. Fraction 2 consisted of almost pure argon, so it was discarded, while fractions 3 to 7 were submitted to further treatment. The course of the operation is shown in Table I: the fractions, which were discarded, are indicated by figures in square brackets: the fractions,  $\frac{2}{3}$ , etc. show the proportions into which the quantities of gas were divided. Fraction 3 was first introduced into the gasholder, and condensed

	[2]	[8]	[14]					
	3	9	(15)	(20)				
1	4	19	16	(22)	24 D	33.07		
	5	11	17	21 $\frac{1}{3}$				
	6	12	18	23 $\frac{1}{3}$	25 lost	27	D	47.55
	7	13	19	-	26	28		
						29 D	56.01	

in the bulb. About  $\frac{2}{3}$  of it was then allowed to evaporate, and the gas was transferred to a tube (8). Fraction 4 was then condensed with the residue and partially evaporated, the first portion of the gas which distilled forming fraction 9. This operation was repeated with fractions 5, 6, and 7, the quantities of gas taken off at each distillation being so graduated that the resulting fractions were all approximately equal; the last fraction was taken off through the pump after removing the liquid air jacket. Fraction 8 was discarded as consisting mainly of argon, and by refractionating numbers 9 to 13 six other fractions were obtained (14 to 19), and of these the first two were rejected after spectroscopic examination.

As the four remaining fractions (16 to 19) solidified at the temperature of liquid air, it was thought that by mixing them with oxygen it might be possible to effect a more rapid and complete separation of their constituents. A single experiment was sufficient to convince us this was not the case, but that the difficulty of manipulation was only increased; the method was therefore abandoned.

Proceeding by the original method fraction 16 was condensed and evaporated into two portions (20, 21); the lighter portion

20, about  $\frac{2}{3}$  of the whole, was rejected. The remaining third (21) was mixed with fraction 17; the gas was condensed and the first fraction (22) was rejected, and the remainder was condensed with fraction 18 and divided into three fractions (24, 25, 26). Fractions 27, 28, and 29 were obtained in the same way.

During the early stages of the fractionation the spectroscope had been the only guide in determining whether a separation of the gases was being effected. Later, however, it became apparent that there were present in the mixture three or more gases whose vapour pressures at the temperature of liquid air were widely different; for while argon could only be liquefied under pressure, the vapour pressure of krypton did not exceed 150 mm., and the remaining gas appeared to be nearly non-volatile.

On account of the readiness with which the two latter condensed it was necessary to take certain precautions usually unnecessary in fractionating gases. If the stem of the fractionation bulb were immersed in liquid air before the gas was introduced the gas condensed in it, and as the liquid air evaporated, the solid volatilised without undergoing fractionation. To overcome this difficulty the vacuum-vessel was supported so that the surface of the liquid air only just touched the bottom of the bulb; when the gas was admitted it condensed in the bulb which was then completely immersed in the liquid air. In fractionating krypton and xenon every fraction of gas was taken off through the pump.

Fractions 24, 25, 27, 28, 29 now consisted of krypton and xenon with but little argon. Of these fractions 25 was unfortunately lost through an accident; 24 had a density 32.07; fractions 27 and 28 appeared to have about the same composition, the mixture had the density 47.55; fraction 29 had the density 56.04.

	-30--	
24 -D=32.07-	-31-	—D=36.6
27 -	-30--	
-D=47.55-	-31-	—D=41.44
28 -	-31-	
	-31-	
29 -D=56.04-	-32--	—D=61.7

Fractions 27 and 28 were mixed together, and each of the three quantities of gas was in turn solidified in the fractionation

bulb, and separated into a lighter and a heavier part. These fractions were mixed as is shown in the table so as to obtain three samples of gas, two of which appeared from their spectra to be nearly pure krypton, while the third of density 61·7 consisted chiefly of xenon. The two lighter fractions were separately solidified and separated into two portions :—

D = 36·6) -	33 $\frac{1}{3}$	Krypton and argon
	34 $\frac{1}{3}$	D = 40·82) Krypton.
D = 41·44	35 $\frac{1}{3}$	D = 40·73) Krypton.
	36 $\frac{1}{3}$	Krypton and xenon

The heavier two-thirds (8 c.c.) of the light gas and the lighter two-thirds (8 c.c.) of the heavy gas had the same density and the same refractivity, and it was therefore concluded that they consisted of one and the same definite chemical substance, to which the name krypton had been given. Further, if the assumption that krypton is a monatomic element is a correct one, its atomic weight is 81·5, and it occupies the position in the periodic table of the elements between bromine and rubidium.

The separation of the xenon from the krypton in fractions 32 and 36 proved more tedious than difficult, for though their vapour pressures at the temperature of liquid air differed very considerably, the krypton appeared to dissolve or become enclosed in the solid xenon, and could only be separated by repeated fractionation. The gas was condensed into the bulb, in the manner already described, and allowed to volatilise into the pump, the exhaustion being continued so long as any gas could be removed. The vessel containing the liquid air was then lowered, and the xenon was collected separately. The lighter fraction (37) was treated in this manner several times till nearly all the

32, 36	37	Krypton with trace of xenon.
	38	Xenon with trace of krypton.

xenon had been removed to fraction 38, which was then subjected to the inverse operation, that is to say, it was condensed, and after taking off traces of krypton through the pump, it was allowed to volatilise, the process being repeated with the heavier

fraction. In this way about 3 c.c. of a gas of density 64 was obtained, and as the density did not increase on further fractionation it was taken to be a pure sample of xenon, the heaviest constituent of atmospheric air. This is confirmed by the fact that the density corresponds to the atomic weight 128, placing xenon between iodine and caesium in the periodic table.

H .	1	He .	3.95	Li .	7
F .	19	Ne .	19.9	Na .	23
Cl .	35.5	A .	39.9	K .	39
Br .	80	Kr .	82	Rb .	85.5
I .	127	X .	128	Cs .	133

4. *The distillation of liquid air.*—Mr. E. C. C. Baly has investigated the relationship of the composition of the liquid and vapour phase of liquid air boiling under constant pressure, and has shown that the equation,

$$\log r' = a + b \log r,$$

in which  $r'$  is the ratio of the components in the liquid and  $r$  the ratio of the components in the vapour, holds good. This equation was first applied by Lehfeldt (*Phil. Mag.* [5], xl. 397) to the results of F. D. Brown (*Chem. Soc. Trans.* xxxix. 304) for the distillation of two liquids; and in Baly's experiments the air is supposed to consist of a mixture of oxygen and nitrogen, the effect of the argon being negligible. The following figures indicate the order of the agreement between the observed and calculated values of ratios of the oxygen to the nitrogen in the vapour phase; they are, indeed, as close as could be desired:—

T (constant-pressure, hydrogen scale).	Ratio observed.	Ratio calculated.
80°	0.136	0.137
82°	0.309	0.310
84°	0.584	0.586
86°	1.09	1.09
88°	2.29	2.30
90°	8.81	8.87

\* The temperatures were determined by means of a Callendar compensated hydrogen thermometer (p. 151). The samples of the vapour were drawn off through a capillary tube close to the surface of the liquid air, which was contained in a vacuum-vessel



plugged with cotton-wool; the oxygen was absorbed by means of phosphorus. At the same time samples of liquid were drawn into a fine capillary tube connected through a wider tube with a water-pump and with a mercury gasholder; the liquid evaporated in the wide tube, and the analysis of the gas drawn into the gasholder gave the composition of the liquid.

Mr. Baly's results may be applied to the determination of the temperature of liquid air from the analysis of its constituents. The method gives very accurate results, and is perhaps the readiest method of checking resistance thermometers, etc., at low temperatures (see p. 239).

### THE VAPOUR PHASE

Temperature (constant- pressure hydrogen)	Percentage of Oxygen.	Temperature (constant- pressure hydrogen)	Percentage of Oxygen.
77.54	0.00 B.P. of Nitrogen.	85.0	41.25
78.0	2.18	85.5	48.17
78.5	4.38	86.0	52.19
79.0	6.80	86.5	56.30
79.5	9.33	87.0	60.53
80.0	12.00	87.5	64.85
80.5	14.78	88.0	69.58
81.0	17.66	88.5	74.37
81.5	21.22	89.0	79.45
82.0	23.60	89.5	84.55
82.5	26.73	90.0	89.80
83.0	29.95	90.5	95.10
83.5	33.35	90.96	100.00 B.P. of Oxygen
84.0	36.86		
84.5	40.45		

### THE LIQUID PHASE

77.54°	0.00	84.5°	69.31
78.0°	8.10	85.0°	72.27
78.5°	15.25	85.5°	75.10
79.0°	21.60	86.0°	77.80
79.5°	27.67	86.5°	80.44
80.0°	33.35	87.0°	82.95
80.5°	38.53	87.5°	85.31
81.0°	43.38	88.0°	87.60
81.5°	47.92	88.5°	89.82
82.0°	52.17	89.0°	91.98
82.5°	55.94	89.5°	94.09
83.0°	59.55	90.0°	96.15
83.5°	62.93	90.5°	98.16
84.0°	66.20	90.96°	100.00

To the separation of the constituents of a liquid by fractional distillation there is a practical limit on account of the extreme difficulty of making the liquid boil as a whole. It was found (*Phil. Trans.* 1901) that when atmospheric nitrogen, condensed in a bulb at the temperature of liquid air, was allowed to evaporate under atmospheric pressure, the composition of the vapour was the same as that of the liquid, and no separation of the neon and helium occurred. When, however, a current of air was blown into the liquid through a capillary tube, the gas which boiled off was rich in the lighter constituents.

In some cases there is also a theoretical limit to the degree of separation which can be effected.

If the vapour pressure of a mixture of two substances at the same temperature  $t$ , be plotted against the quantity of one of them which is present in the liquid, the curve may have the form represented by  $a$ ,  $b$ , or  $c$ . The curve  $b$  represents the case in which, as the vapour pressure rises, the concentration of one constituent in the liquid continually increases. The majority of mixtures, including air, follow this rule; they are all capable of being more or less completely separated into their constituents. The curve  $a$  represents the case in which a mixture of two liquids at a certain temperature has a greater vapour pressure  $p$  than either of its constituents. In this case, if the mixture were allowed to evaporate at the pressure  $p$ , the liquid would boil at temperature  $t$ , and the distillate would have a constant composition corresponding to that which gave the maximum pressure; the residue would consist of the higher boiling constituent. The curve  $c$  represents the inverse set of conditions.

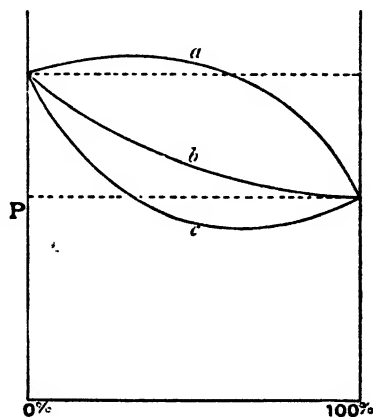


FIG. 110.

By altering the pressure and consequently the temperature of ebullition of the liquid, the relationship between the composition of the liquid and vapour phases will be changed. Consequently, though it may be impossible to obtain an efficient separation of the constituents under one set of conditions, it may

be possible to do so under another. Unfortunately, little work has been done in this direction, and so far only organic liquids and water have been investigated. Liquefied gases should lend themselves readily to this investigation, as it would be possible to obtain direct analyses of the liquid and of the vapour, and to determine the vapour pressures and the heats of evaporation of the liquids. These data would be at least sufficient for a partial solution of the problem.

## CHAPTER XVII

### VAPOUR PRESSURE AND CRITICAL CONSTANTS

The determination of vapour pressures—The compression apparatus—Standardising high pressure gauges—Introduction of gases and liquids into the compression tubes—Calculation of the results—The law of Ramsay and Young—Vapour pressures of water and methyl alcohol—Vapour pressures, boiling-points, melting-points, critical constants, etc., of oxygen, ozone, nitrogen (chemical and atmospheric), ethylene, methane, nitric oxide, nitrous oxide, carbon monoxide, carbon dioxide, and ammonia—Table of constants for the commoner gases—Determination of the critical constants—The critical temperature and pressure—The critical volume by the methods of Cailletet and Mathias, and of Young.

THE vapour pressures of liquefied gases may be determined by one of two methods; either the liquid may be allowed to evaporate and its temperature determined by means of a thermometer immersed in it; or the gas may be condensed in a bulb, which is connected with a manometer and maintained at constant temperature by immersion in a bath of liquid, preferably boiling under constant pressure.

The first method can only be carried out with considerable quantities of the gas, and even if a platinum resistance thermometer is used, it is difficult to reduce the quantity to less than two or three litres. The method has a distinct advantage in dealing with mixtures, and it would be very difficult to measure the vapour pressure of such a substance as liquid air by the second method, for unless the temperature remained very constant for a considerable time the condition of equilibrium between the vapour and the liquid would never be arrived at. This method was employed by Olszewski, Estreicher, and Baly in determining the boiling-points of nitrogen and oxygen, and by the latter in determining the relationship between the composition and boiling-points of mixtures of the two (see p. 224).

The second method was employed in the determination of the vapour pressure of argon, etc. For pressures up to 800 mm. an open manometer was used; for higher pressures it was necessary to employ a compression apparatus which will be described later.

The apparatus employed in the determination of vapour pressures up to 800 mm. closely resembled the apparatus used

in fractionating the liquefied gases. The bulb A, in which the gas was condensed, communicated with the gasholder B, with the pump through the stopcock C, and with the manometer D. The pressure could be adjusted by raising or lowering the reservoir E by means of a string which passed over a pulley; the levels of the surface of the mercury in the two tubes was determined by reference to a silvered glass scale placed behind them.

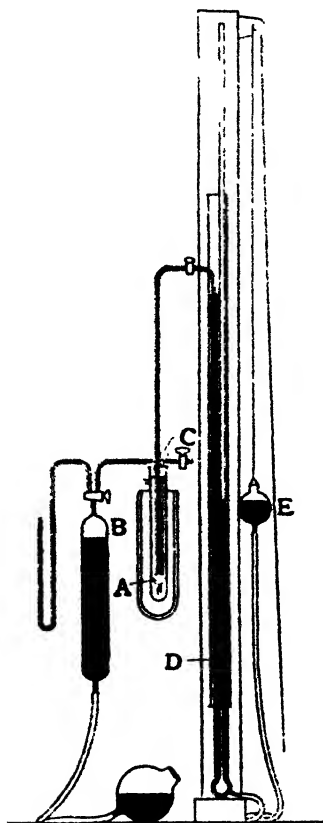


FIG. 111.

After thoroughly exhausting the apparatus the gas was introduced into the gasholder B, and liquefied or solidified in the bulb A, which was immersed in liquid air or some other refrigerant; the temperature was determined by a platinum resistance or hydrogen thermometer. In order to test the purity of the gas, it was usual to take readings with the mercury in different positions in the manometer tube. If a change of volume did not produce a change in

pressure the gas was taken to be pure; otherwise small quantities of gas might be taken into the pump through the stopcock E till the pressure of the remainder became constant, or it was necessary to reject the sample of gas.

In determining the vapour pressure of a liquefied or solidified gas, at the temperature of pure liquid surrounding the bulb and boiling under atmospheric pressure, no difficulty was experienced, and very concordant readings could be obtained. It was not,

however, possible to determine the vapour pressures accurately if the temperature was rising rapidly, since the rate of evaporation of the liquid or solid did not keep pace with the rise of temperature of the bath. The flow of heat across the walls of the bulb is not rapid enough to compensate for the heat lost by evaporation, and the liquid or solid and the vapour never arrive at a condition of equilibrium. This was particularly marked at temperatures below the melting-point of the substance under examination. It was also noticed that in determining the vapour pressure of solid argon at about 8.00 mm. pressure using a bath of liquid air, that it was difficult to obtain very concordant readings. It appeared that the pressure varied fairly rapidly with the temperature, and the irregularity was caused by the superheating of the liquid air.

#### THE DETERMINATION OF THE VALUES OF $PV$ AT HIGH PRESSURES, AND OF VAPOUR PRESSURES, CRITICAL CONSTANTS, ETC.

*The compression machine.*—A convenient form of compression apparatus, which may be employed for the determination of vapour pressures, critical points, etc., has been described by Ramsay and Young, and more recently modified by the latter. It may be used up to 200 atmospheres, or even higher, without difficulty; but the volume of gas which can be compressed is limited, of course, by the size of the plunger.

The body of the instrument (Fig. 112) consists of a wrought-iron barrel, with openings  $a$ ,  $a'$ ,  $a''$  to receive the compression tubes. Two of the openings are at the top, the third  $a''$ , is at the side, but by means of an attachment  $b$ , it may be made to serve the same purpose as  $a$  and  $a'$ . The openings are closed by caps fitted to them by means of well-cut screws. Holes in the caps admit of the passage of the capillary compression tubes or manometers. The pressure is applied by means of a screw  $f$  and a cylindrical plunger  $d$ . The latter, working between guide bars  $e$ , passes through the cap  $g$ , which serves as a gland, into the interior of the apparatus.

• The compression tubes and manometers are made by sealing capillary tubes to tubes of about 8 mm. in diameter, which are drawn out at the lower end (Fig. 113). The tubes should be of lead-glass, which is usually more uniform than soda-glass; a line of white enamel on the back of the tubes facilitates observation.

The tubes can be graduated and calibrated from the closed end in the manner described on p. 76. The volumes may be expressed in grams of mercury or in cubic centimetres.

*The manometers.*—It is usual to employ two manometers, one reading pressures up to about 10 atmospheres and one reading pressures up to 50 or 60 atmospheres. In each case the capillary portion should be about 500 mm. long, and should have an internal diameter of about 0.8 mm. The wider tube at the bottom of the high-pressure gauge should have a capacity of about 2 c.c. Both manometers may be filled with dry air.

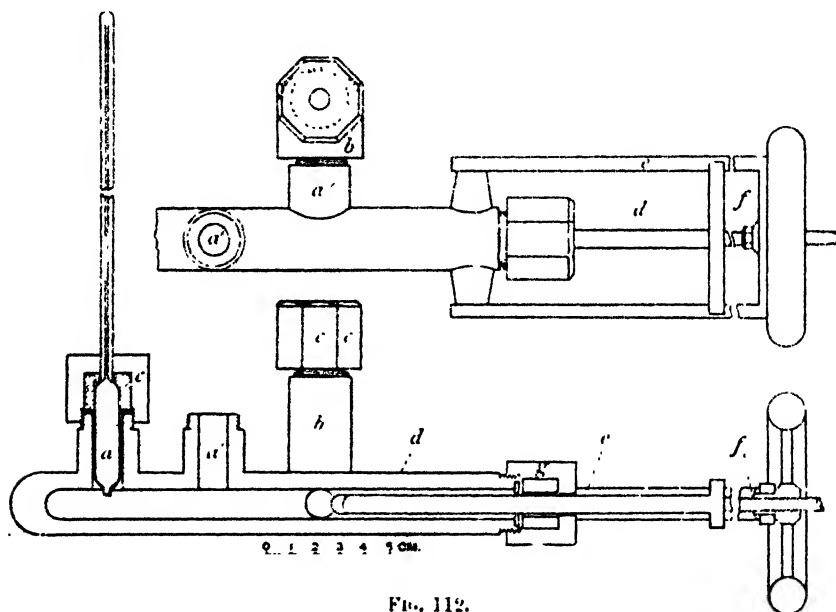


FIG. 112.

for which the values of  $pv$  have been accurately determined by Amagat (p. 166).

The compression tube to contain the gas whose compressibility or vapour pressures are to be determined is of the same form as the high-pressure manometer. The wide tube should also be drawn out at the open end, so that it may be sealed to an apparatus for introducing the gas (p. 300). In the determination of the vapour pressures at low temperatures the capillary portion of the tube should be bent on itself.

Before the gas is introduced into the manometer or compression tube the latter is fitted into the cap in the following manner.

A cylinder of rubber is cut from a rubber stopper by means of a large cork borer, so that it exactly fits the cavity in the cap and fills it to within about 3 mm. of the surface. A hole of exactly the same diameter as the wider portion of the capillary tube is bored nearly through the cork and is continued, as in the figure, by means of a smaller cork-borer, to allow for the passing of the capillary tube; both holes must be truly central. A washer of hard leather, previously heated on a water bath in a flask containing tallow, is placed above the rubber, and a worm of hard beeswax is twisted round the glass tube close to the washer.

The cap *g* through which the plunger passes is also packed with rubber, but the plunger itself is surrounded with a layer of thin leather thoroughly soaked in grease. If this precaution is not taken the plunger may adhere to the rubber, which will in consequence rapidly wear away.

To introduce air or any other gas into the compression tubes or manometer, after fitting it into the screw-cap of the compression apparatus, it may be sealed to the apparatus for introducing gases into vacuum tubes. After exhaustion, the gas is introduced at a slightly reduced pressure, and the compression tube is sealed off with a hand-blowpipe. The volume of gas in the tube can, if necessary, be determined by measuring the volume of gas let into the apparatus and the volume removed through the pump. This operation is, however, somewhat difficult to carry out with accuracy. It must not be forgotten that the introduction of too great a quantity of gas might render it impossible to compress the gas into the capillary portion of the tube at all. The point of the tube can easily be broken off below the surface of the mercury in the compression apparatus before the cap is screwed home.

This method is not usually employed in filling the gauges with air. The open end of the gauge is attached by a piece of rubber tube, through tubes containing pentoxide of phosphorus and soda lime, to the pump. After exhausting the tube and admitting air two or three times, the rubber tube is



FIG. 113.



rapidly removed and the open end of the gauge is plunged below the surface of the mercury in the compression apparatus.

If the substance is a liquid at the ordinary temperature of the air it is necessary to proceed somewhat differently. The quill tube *c* (Fig. 112), is blown into a bulb and drawn out again at *c*. A small quantity of liquid is placed in the tube, and while the liquid is boiling it is sealed at *c*. The greater part of the liquid is then distilled out of *a* and *b*, and condenses in *c*, which is cooled; when sufficient liquid is left in *c* the tube is sealed at *d*. The point of the tube is broken beneath the surface of the mercury in the compression apparatus in the manner already described.

After the two manometers are placed in position a vertical capillary tube, about 1.5 metres in length, is fitted into the third cap, which is screwed on to the apparatus. This serves as an open manometer for determining the values of the product  $pv$  for the low-pressure manometer. The manometers are enclosed in tubes through which a current of water circulates, the temperature being determined by means of a thermometer in one of them. The pressures are read off on a scale placed behind the vertical tube, and the difference of level of the mercury in the open and closed (low pressure) manometers is determined by reading with a telescope the point of the scale corresponding to the first graduation on the manometer, which is usually divided in millimetres. Observations are usually taken with rising and falling pressure, and before each reading the apparatus is hammered with the hand to bring the mercury in the capillary tube into adjustment. The following are the results of an experiment.

Barometer, 747.2 mm.

Difference of levels—325.2 on scale = 710.0 on manometer.

Manometer reading (millimetres).	Volume of air.	Temperature <i>t</i> of manometer (absolute).	Volume of air corrected to 0° C.	Open manometer reading.	Difference of levels of the two scales.	Temperature of mercury column.	Pressure in terms of mercury at 0° C.	$PV \times 10^6$ .	Pressure re-calculated from mean $PV$ .
328.6	.17442	285.93°	.16653	677.7	- 3.4	16.4° C.	1417.5	23,606	1423.2
346.7	.18393	285.75°	.17571	584.4	+ 21.5	..	1349.2	23,707	1348.5
369.6	.19619	...	.18743	477.6	+ 44.4	...	1265.5	23,714	1261.4
400.1	.21220	285.72°	.20275	351.7	+ 74.9	...	1174.4	23,812	1168.9
442.3	.23279	...	.22242	198.4	+ 117.1	...	1059.7	23,570	1065.5
481.7	.25577	...	.24438	70.0	+ 156.5	...	970.9	23,727	969.8
503.7	.27494	..	.26270	18.5	+ 178.5	...	904.6	23,764	902.2

Mean value of product  $pv = 237\cdot00$ .

The figures in the last column indicate the order of accuracy of the experiment.

This set of observations serves to standardise the low-pressure gauge, which can now be compared with the high-pressure gauge, to determine the value of  $pv$  for the latter. For this purpose the open manometer is removed, and is replaced either by the compression tube containing the gas to be examined, or by a plug of glass. The pressure is then raised till the mercury enters the capillary tube of the high-pressure gauge, and a series of simultaneous readings of the volumes of the two gauges are taken. It is necessary to apply a correction for the difference of level between the surfaces of the mercury in the two gauges, but if the two are at the same temperature no other correction is necessary. The results of a set of observations are stated in the following table:—

High-pressure manometer reading.	Volume of air in grains of mercury.	Low-pressure manometer reading.	Volume of air in cubic centimetres.	Temperature of manometers.	Observed pressure from low pressure manometer.	$PV \times 10^2$ .
84.5	2.4172	45.0	.02790	285.85°	9.358	21,595
105.4	2.2327	40.8	.02572	285.85°	10.096	21,520
132.3	1.9985	35.35	.02288	285.85°	11.273	21,508
157.1	1.7816	30.6	.02071	285.85°	12.389	21,514
179.8	1.5825	26.0	.01802	285.8°	14.154	21,396
153.0	1.8175	31.3	.02078	285.85°	12.352	21,434
84.7	2.4145	45.0	.02790	285.9°	9.356	21,536
63.3	2.5597	49.5	.03011	285.85°	8.721	21.600

Mean value of  $pv = 215\cdot12$ .

In the case of the high-pressure manometer the high figures correspond to small volumes, while the inverse is the case with the low-pressure gauge. The difference of the levels of the mercury in the two gauges may be deduced from the observation that the mark 33.2 on the high-pressure gauge corresponds to the mark 25.8 on the low-pressure gauge. The figures in the sixth column are calculated from the formula,

$$P = \left\{ \frac{PV \text{ (for low-pressure gauge)}}{\text{Observed volume} \times \frac{273}{T}} + \text{Correction} \right\}$$

It is unnecessary to apply a further correction to reduce the observed pressures to actual pressures, since we wish to calculate the product

$$(\text{volume}) \times (\text{observed pressure})$$

for the high-pressure gauge.

The most convenient way in which the correction can be applied is as follows:—The reciprocals of the volumes are calculated from the values of  $PV$  for air as given by Amagat:—

P. (mm.)	$\frac{1}{V}$	$\frac{1}{V}$
5,000	5,011	11
10,000	10,049	49
15,000	15,113	113
20,000	20,202	202
25,000	25,314	314
30,000	30,441	441
35,000	35,582	587
40,000	40,712	717
45,000	45,851	851
50,000	50,995	995
55,000	56,098	1098
60,000	61,199	1199

The figures in the third column stand for the amounts in millimetres to be subtracted from the observed pressures, the reciprocals of the volumes, in order to determine the true pressure. The figures in the second and third columns may be plotted on a curve.

The determination of the vapour pressure of a liquid confined under high pressure in the apparatus just described, is a comparatively simple matter so long as the compression tube can be maintained at a fairly constant temperature. The tube can be surrounded by a water-jacket, or by the vapour of a liquid boiling under constant pressure in the apparatus described in the Appendix. For low temperatures the end of the tube, which is bent downwards, may be immersed in a liquefied gas which may be allowed to evaporate into a gasholder; the temperature may be determined by means of a gas thermometer or resistance coil. When working at low temperatures it is very necessary to take care that the mercury is not forced into that part of the tube which is cooled below its freezing-point.

In determining the vapour pressure, after the temperature has become fairly constant the pressure should be raised until some of the gas has become condensed in the tube. The apparatus should then be thoroughly hammered with the hand to allow the mercury in the gauges to settle into position, and after sufficient time has elapsed for the vapour and the liquid to arrive at a condition of equilibrium, the gauges are read. The pressure may be calculated from either or from both of the gauges. If the temperature is fairly constant it should be possible to make two or more observations of the pressure, changing the volume of the vapour in the compression tube between each observation. It may be noted here that in the case of water Ramsay and Young found that the vapour pressure depended upon the volume of liquid in the compression tube: this is probably due to the existence of some difference between the nature or composition of the surface, and of the mass of the liquid, and may be connected with the fact that water is an associated liquid.

The following figures indicate the method of calculating the vapour pressure from the readings of one of the gauges. They represent the vapour pressure of argon at the temperature of boiling nitric oxide.

Gauge reading.	Temperature.	Volume.	$\frac{PV}{r}$ at 0° C.	$\Delta$	$c$ .	P.
119.0	284.55°A	2.1157	10,596 mm.	- 236	- 54	10,306
122.5	„	2.0846	10,781 „	- 402	- 57	10,322
118.7	„	2.1168	10,592 „	- 226	- 54	10,312

Here  $\Delta$  stands for the difference of the level of the mercury in the manometer and compression tube, and since the volume of vapour and liquid was changed between the observations it is not a constant. The correction  $c$  which is subtracted from the observed pressure to reduce it to the actual pressure is obtained from the curve referred to on p. 234.

*Calculation of the vapour pressure of liquids.*—Ramsay and Young (*Phil. Mag.*, 1886, **21**, 33) have shown that the vapour pressures of any liquid may be calculated for any temperature

when the vapour pressures corresponding to two temperatures are known.

Let  $Ta$  and  $Tb$  be the temperatures corresponding to the vapour pressure  $p$  for two liquids, and  $Ta'$  and  $Tb'$  the temperatures corresponding to the vapour pressure  $p'$  for the same pair of liquids.

Thus : —

$$\frac{Ta}{Tb} = \frac{Ta'}{Tb'} + k(Ta - Ta')$$

when  $k$  is some constant.

Methyl alcohol or water, liquids for which the vapour pressures have been accurately determined over a wide range of temperature, may be taken on one side, and on the other the substance for which only a few points have been found. The accuracy, of course, increases with the number of known points, for it is then possible to plot the results on curve paper, and redetermine the pressures or temperatures from the smoothed ratios. In the following plate the absolute temperatures of water corresponding to the definite vapour pressures are made the ordinates, and the ratios corresponding to those temperatures are made the abscissae.

In the following table the observed vapour pressures corresponding to certain absolute temperatures for krypton are given together with the corresponding absolute temperatures for water and methyl alcohol, and the ratios which have been calculated from them. The results are plotted on the accompanying plate in the manner indicated above.

P.	TKr.	Taq.	TKr. Taq.	Tal.	TKr. Tal.
386.6	112.7	355.1	0.3174	321.8	0.3502
898.7	123.1	377.5	.3264	342.3	.3596
11,970	170.9	474.3	.3603	329.3	.3981
28,808	197.9	521.2	.3797	471.4	.4198
30,837	201.0	525.1	.3828	475.0	.4229
31,621	201.5	526.6	.3826	476.4	.4230
34,693	204.1	532.2	.3835	481.4	.4240
37,006	206.4	536.2	.3849	485.0	.4256
41,245	210.5	544.3	.3876	491.0	.4287

In order to plot the vapour pressure curve for krypton, the absolute temperatures of water corresponding to definite

intervals of pressure were first determined, and the ratios corresponding to these temperatures were read off on the plate;

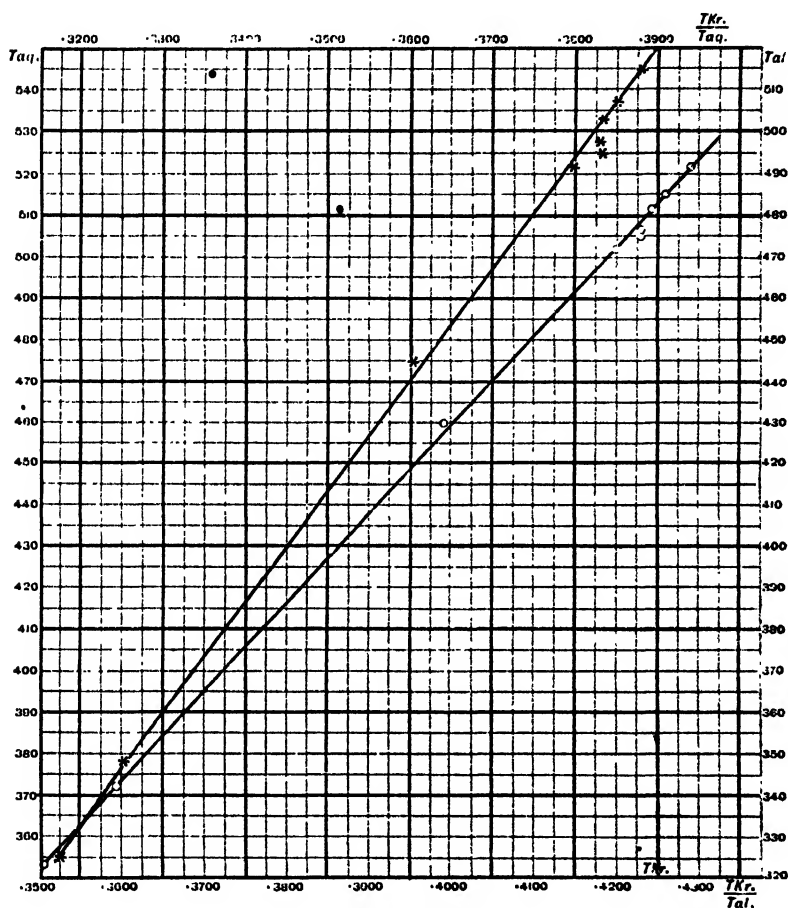


FIG. 114.

the ratios multiplied by the absolute temperatures for water gave the absolute temperatures for krypton corresponding to the same pressures.

$p$ . (mm.)	$T_{aq.}$	$TKr.$ $T_{aq.}$	$TKr.$
400	356.0	.3198	113.8
600	366.5	.3229	118.35
900	374.6	.3257	122.0
1,200	380.6	.3280	124.8
1,500	390.8	.3315	129.55
2,000	402.6	.3359	135.2

P. (mm.)	Taq.	TKr. Taq.	TKr.
4,000	427·2	·3449	147·3
6,000	443·3	·3507	155·5
8,000	555·8	·3553	161·95
10,000	465·9	·3591	167·3
16,000	488·7	·3672	179·45
20,000	500·4	·3717	186·0
30,000	523·6	·3801	199·0
40,000	541·1	·3865	209·1
41,300	critical point)		210·5

The figures in the first and last columns plotted as ordinates and abscissæ give the vapour pressure curve. It is noticeable that the curve can be continued above the critical point, but it has no real significance.

*Vapour pressure of water.*—The vapour-pressures at temperatures between  $-20^{\circ}$  C. and  $120^{\circ}$  have been calculated by Broch from Regnault's determinations: they are to be found in every large text-book of physics. The vapour pressures at higher temperatures have been determined by Ramsay and Young (*Phil. Trans.*, 1892, 183A, 112).

#### VAPOUR PRESSURE OF WATER

T. Abs.	P. (mm.)	T. Abs.	P. (mm.)
393°	1484	473°	11,625
403	2019	483	14,240
413°	2694	493°	17,365
423°	3568	503°	20,936
433°	4652	513°	25,019
443°	5937	523°	29,734
453°	7487	533°	35,059
463°	9403	543°	41,101

The vapour pressures of methyl alcohol have been determined over wider ranges, and are therefore often useful (Ramsay and Young, *Phil. Trans.* 1887, 137, 326). They are as follows:—

## VAPOUR PRESSURES OF METHYL ALCOHOL

T. Abs.	P. (mm.)	T. Abs.	P. (mm.)
253°	7.605	433°	12,999
263°	15.402	443°	16,213
273°	29.600	453°	20,016
283°	54.224	463°	24,481
293°	95.104	473°	29,688
303°	160.28	483°	35,722
313°	260.47	493°	42,676
323°	409.47	498°	46,530
333°	625.10	503°	50,651
343°	926.6	505°	52,378
353°	1,340.3	507°	54,151
363°	1,894.6	509°	55,971
373°	2,622.5	510°	56,900
383°	3,561.1	511°	57,839
393°	4,751.3	511.5°	58,310
403°	6,239.2	512°	58,790
413°	8,072.5	512.5°	59,268
423°	10,306	513°	59,759

*Oxygen*.—The boiling-point on the constant-volume hydrogen scale has been determined by Wroblewski, 90.6 (Weiner Akad. 1888); Olszewski, 90.6; Ladenburg and Krugel, 90.7; and Dewar, 90.3 to 91.5.

The vapour pressures of oxygen have been determined by Olszewski, Estreicher, and Baly. Olszewski's measurements extend from 62° Abs. to the boiling-point, which was determined both by the hydrogen and by the helium thermometer (see p. 156). Measurements at higher pressures (*C. r.* 100, 351) were also carried out; the observed temperatures appear to be about half a degree too high. Estreicher's measurements are very erratic, but are sufficiently numerous to give an idea of the trend of the curve. Baly's experiments cover only a limited range; the temperatures were determined by means of a Callendar thermometer (p. 151). The smoothed results, which appear to be about 0.5° too low, are given in the following table:—

[TABLE



Temperature (constant- pressure (B.), constant- volume (Ols. and E.))	Vapour-Pressure.		
	1. (B.)	2. (Ols.)	3. (E.)
62	...	8.4	9.6
63	.	10.8	11.0
64	.	13.3	11.6
65	...	16.1	17.7
66	...	19.7	21.2
67	.	24.0	25.6
68	.	29.1	31.0
69	...	35.6	37.2
70	...	43.0	44.6
71	.	51.6	53.0
72	.	61.0	62.5
73	.	72.0	73.5
74	.	85.0	86.0
75	.	100	100
76	.	117.5	116.0
77.0	138.4	136.2	134
77.5	158.7	146.5	145.1
78.0	170.0	158.0	155.7
78.5	181.4	169.8	167.5
79.0	193.5	182.5	180.0
79.5	206.6	195.9	193.9
80.0	220.0	210.1	208.1
80.5	234.0	224.8	222.8
81.0	249.0	240.1	237.9
81.5	264.8	257.0	253.7
82.0	281.8	274.0	270.0
82.5	299.5	292.1	287.5
83.0	319.2	311.7	305.3
83.5	338.6	332.0	323.3
84.0	359.0	353.5	342.3
84.5	380.5	376.4	362.0
85.0	401.8	401.7	382.9
85.5	424.6	427.0	404.6
86.0	449.0	454.0	427.4
86.5	475.5	482.0	451.7
87.0	503	510.5	477.0
87.5	530.5	540.5	506.5
88.0	560.0	571.6	538.6
88.5	590.0	604.7	571.5
89.0	621.5	639.9	608.8
89.5	653.6	676.6	646.5
90.0	687.5	714.2	685.0
90.5	725.5	753.2	725.5
91.0	761.5	794.0	766.0

Olszewski's measurements at higher pressures are as follows

T. (Abs.)	P. (mm.)
154.2° (Critical)	44,080
153.5°	37,772
151.4°	35,492
150.4°	34,580
149.0°	32,680
147.4°	30,704
146.2°	28,956
145.0°	27,588
144.0°	26,144
142.7°	24,776
126.0°	10,412
124.4°	9,348
121.4°	7,782
116.4°	6,355
113.1°	4,735
106.9°	3,230
97.6°	1,642
91.6°	760

Later results appear to indicate that the boiling-point of oxygen on the constant-volume hydrogen scale is 90.5°.

*Ozone*.—Troost (*C. r.*, 1898, 126, 1781) and Ladenburg (*Ber.*, 1893, 2508) have succeeded in obtaining fairly pure liquid ozone by condensing ozonised oxygen and subsequently evaporating the liquid. They give 154° Abs. and 148° Abs. respectively as the lower limiting value for the boiling-point. The experiment is a dangerous one, though Troost states that liquid ozone is non-explosive in the absence of organic matter.

By passing ozonised oxygen into a vacuum-vessel in which a test-tube of liquid air is suspended, the ozone may be condensed to a blue liquid, which collects in drops on the outside of the test-tube.

*Nitrogen*.—The measurements of the vapour pressure of atmospheric nitrogen by Olszewski (*C. r.*, 99, 134; 100, 350) and Baly (*loc. cit.*) show a very close agreement. Olszewski's experiments cover a wider range; the critical point was found to be 124° A. and the melting-point 59° A. at 60 mm. pressure; the constant-volume hydrogen thermometer was employed. The temperatures in Baly's experiments are on the constant-pressure hydrogen scale. The following table contains the results smoothed by the method of Ramsay and Young:—

Temperature.	Pressure in mm.		
	Baly.		Olszewski (Atmospheric).
	Atmospheric.	Chemical.	
77	716·0	717·0	726·0
77·5	757·5	760·0	768·5
78	800·0	806·0	815·0
78·5	846·5	856·0	860·5
79	895·0	906·0	908·5
79·5	944·0	959·0	959·0
80	995·0	1013·0	1,010·5
80·5	1048·0	1072·5	1,065·5
81	1104·0	1130·5	1,121·5
81·5	1163·0	1193·0	1,186·0
82	1225·4	1258·0	1,240·5
82·5	1290·0	1324·0	1,304·0
83	1357·0	1386·0	1,369·5
83·5	1426·0	1468·0	1,438·0
84	1497·0	1544·5	1,508·5
84·5	1570·5	1623·5	1,582·0
85	1646·0	1705·5	1,658·0
85·5	1725·0	1792·0	1,737·0
86	1808·0	1880·0	1,820·0
86·5	1895·0	1968·0	1,904·5
87	1985·0	2062·0	1,992·5
87·5	2076·0	2146·0	2,081·0
88	2170·0	2256·0	2,173·5
88·5	2267·0	2310·0	2,268·0
89	2368·0	2465·0	2,368·0
89·5	2472·5	2575·5	2,472·0
90	2581·0	2686·0	2,579·0
90·5	2694·0	2799·0	2,688·0
91	2812·0	2916·5	2,802·0
92·4	...	...	3,125·0
94·1	...	...	3,581·0
95·9	...	...	4,084
97·6	...	...	4,652
99·4	...	...	5,274
101·2	...	...	5,962
103·0	...	...	6,717
104·9	...	...	7,546
106·7	...	...	8,644
108·6	...	...	9,443
110·4	...	...	10,520
112·3	...	...	11,689
114·3	...	...	12,956
116·2	...	...	14,325
118·1	...	...	15,801
120·1	...	...	17,390
122	...	...	19,097
124 (Critical)	...	...	20,926

*Ethylene.*—The boiling-point of ethylene has been found by Olszewski (*C. r.*, 99, 133) and by Ramsay and Travers to be

170.5° Abs. When, however, the ratios of the corresponding temperatures of water and ethylene, as determined by Olszewski, are plotted, the ratios corresponding to the lower pressures lie on a line which does not include the ratio corresponding to the boiling-point. It appears, therefore, probable that either the boiling-point is incorrect or the temperatures corresponding to the lower pressures are affected by a constant error. The following values for the vapour pressures are calculated from the observed temperatures of boiling ethylene, measured by means of a Callendar constant-pressure hydrogen thermometer. The results are probably 1 too low.

P. (mm.)	T. (Abs.)	P. (mm.)	T. (Abs.)
100	143.8°	500	164.1°
200	151.9°	600	166.8°
300	157.0	700	169.2°
400	160.8	760	170.5°

Wroblewski (*Wien. Akad.*, 1888) and Witkowski (*Phil. Mag.*, 1896, 1) found the boiling-point to be 169.5° on the constant-volume hydrogen scale; this result appears to be correct.

The melting-point of ethylene is about 90° Abs., and consequently the liquid may be used as a refrigerant over a very wide range of temperature.

*Methane.*—The results obtained by Olszewski (*C. r.*, **100**, 940) when smoothed by the method of Ramsay and Young appear fairly concordant. The following values have been calculated from them:—

P. (mm.)	T. (Abs.)	P. (mm.)	T. (Abs.)
500	103.6°	15,000	160.5°
760	108.3°	20,000	167.9°
1,000	111.6°	25,000	174.4°
2,000	121.2°	30,000	180.1°
4,000	132.2°	35,000	184.9°
6,000	139.7°	40,000	189.4°
8,000	145.7°	42,400	191.2° (Critical)
10,000	150.6°		

Ramsay and Travers find the boiling-point to be 112.7° Abs.

*Nitric oxide.*—The results obtained by Olszewski for the vapour pressures of nitric oxide are somewhat peculiar. When the vapour-pressure curve is plotted it is found that it cuts the curve for methane, which should not occur in the case of simple

substances. Further, the ratios of the corresponding absolute temperatures (p. 236) for nitric oxide and methyl alcohol, when plotted against the methyl alcohol temperatures, do not lie on a straight line, and the boiling-point determined by extrapolation (p. 237) from the pressures at the higher temperatures is found to be  $127.6^{\circ}$  (Abs.) instead of  $120.0^{\circ}$  which was the observed temperature. The gas was prepared by heating ferrous sulphate with nitric acid, but it is probable that the sample examined contained nitrogen, an idea which is supported by the high critical pressure assigned to the gas. It is possible, though improbable, that the irregularities are due to association taking place at low temperatures. The following are Olszewski's results:—

P. (mm.)	T. (Abs.)	P. (mm.)	T. (Abs.)
18	$96.5^{\circ}$	24,316	$163.0^{\circ}$
138	$106.0^{\circ}$	31,160	$168.0^{\circ}$
760	$120.0^{\circ}$	37,924	$172.1^{\circ}$
4,104	$135.0^{\circ}$	43,928	$175.5^{\circ}$
8,056	$144.0^{\circ}$	54,112	$179.5^{\circ}$
15,200	$154.0^{\circ}$		

The boiling-point, as determined by Ramsay and Travers, is  $123.1^{\circ}$  Abs. The gas was liquefied by means of liquid air, and purified by fractional distillation. The temperature was determined by means of a platinum resistance thermometer, which had been standardised by direct comparison with a constant-pressure hydrogen thermometer (p. 151). The temperature remained constant so long as the coil was immersed in the liquid. It may be noted that a minute trace of the higher oxide is sufficient to give a blue colour to the liquid.

*Nitrous oxide*.—Ramsay and Shields (*Chem. Soc. Jour.*, 1893, **63**, 135) have determined the boiling- and melting-points by means of the constant-volume hydrogen thermometer.

Melting-point	. . . .	$170.3^{\circ}$ Abs.
Boiling-point	. . . .	$183.2^{\circ}$ „

The vapour pressures were determined by Faraday in 1845, but the results are worthless.

Cailletet and Mathias (*Jour. de Physique* [2], **5**, 549) determined the volume of the liquid and vapour at temperatures between  $273^{\circ}$  and  $305^{\circ}$  Abs. The critical point, according to their results, is  $310^{\circ}$  Abs.

*Carbon monoxide*.—Olszewski (*C. r.*, **99**, 706). The following are the values of the vapour pressures calculated by the method of Ramsay and Young from Olszewski's results :—

P. (mm.)	T. (Abs.)	P. (mm.)	T. (Abs.)
760	83.0°	10,000	119.2°
2,000	92.7°	15,000	128.3°
4,000	106.9°	20,000	133.2°
6,000	111.4°	25,000	135.8°
8,000	115.1°	25,400	137.4° (Critical)

*Carbon dioxide*.—It is somewhat strange that the vapour pressures of carbon dioxide have never been accurately determined. In Andrews's observations the pressures were calculated on the assumption of Boyle's law: and since the gas certainly contained a trace of air, the results, even if corrected, would be of little value. Andrews gives 303.98 Abs. as the critical temperature, and 73 atmospheres as the critical pressure; the pressure corrected for the deviation of  $p_v$  from unity is probably about 54,400 mm.

Amagat (*Jour. de Physique* [3], **1**, 388) gives the following values for the critical constants:  $T_c = 304.35$ ,  $P_c = 5540.4$ ,  $V_c = 0.464$  cc. Cailletet and Mathias (*Jour. de Physique* [2], **5**, 549) obtained about the same value for the critical temperature.

Cailletet (*C. r.*, **112**, 1170) gives the vapour pressures between  $-80$  and  $-34$  C.:—

P. (mm.)	T. (Abs.)	P. (mm.)	T. (Abs.)
760	193° (Solid)	4159	223°
1178	299°	6627	229°
1681	203°	7790	233°
2356	209°	9652	239°
2964	213°		

When these results are plotted, they appear somewhat irregular.

The melting-point, which lies some little way above the boiling-point, does not appear to have been determined.

A mixture of solid carbonic acid and ether has a constant temperature  $194.8^\circ$  Abs. so long as it has the consistency of butter; as soon as ether appears at the surface the temperature rises (Olszewski).

The densities of liquid carbon dioxide have been determined by Cailletet and Mathias :—

T. (Abs.)	Density.
303·2	0·3507
301·1	0·3044
298·0	0·2543
292·7	0·2014
286·6	0·1585
275·2	0·1040

*Ammonia*.—The vapour pressures have been determined by Pictet for temperatures between  $-30$  and  $+50$  C. The results, when plotted by the method of Ramsay and Young give a fairly straight line. The following are the smoothed results :—

P. (mm.)	T. (Abs.)	P. (mm.)	T. (Abs.)
760	236·0	4,000	279·3
800	241·3	6,000	290·3
1000	245·8	8,000	299·9
1200	249·7	10,000	307·4
1500	254·8	12,000	313·7
2000	261·4	14,000	319·4
3000	271·5	16,000	324·3

The results obtained by Blümke appear to be less reliable. The vapour pressures at higher temperatures can be obtained by extrapolating on Pictet's observation by means of the formula—

$$T_{NH_3} = T_{CH_3OH}(0·64071 + T_{CH_3OH} \times 0·00021318),$$

where  $T_{CH_3OH}$  is the temperature of methyl alcohol corresponding to the pressure required.

Vincent and Chappins give for the critical constants—

Critical temperature	=	404° Abs.
Critical pressure	=	83,800 mm.

*Helium, neon, argon, krypton, and xenon*.—Dewar states that the helium cannot be condensed at the melting-point of hydrogen. At the boiling-point of liquid hydrogen neon appears to solidify (R. and T.) (p. 218), and to have a very low vapour pressure; its critical temperature lies below  $-210^\circ$  C. The following are the smoothed values for the vapour pressure of the three remaining gases (Ramsay and Travers, *Phil. Trans.*, 1901):—

PRESSURE. Min.	TEMPERATURE. (Constant-pressure hydrogen.)			PRESSURE. Min.	TEMPERATURE. (Constant-pressure hydrogen.)		
	Argon.	Krypton.	Xenon.		Argon.	Krypton.	Xenon.
300	78·94°	110·48°	148·9°	14,000	129·47°	175·88°	238·7°
400	81·31°	113·84°	153·2°	16,000	132·73°	179·45°	243·7°
500	83·32°	116·14°	156·8°	18,000	134·88°	182·79°	248·3°
600	84·89°	118·35°	159·7°	20,000	137·36°	186·00°	252·6°
700	86·38°	120·19°	162·0°	22,000	139·65°	188·88°	256·6°
760	...	...	...	24,000	141·80°	191·68°	260·2°
800	87·77°	122·01°	164·7°	26,000	143·82°	194·32°	263·8°
1,000	89·40°	124·84°	168·8°	28,000	145·80°	196·72°	267·2°
1,500	93·52°	129·55°	176·8°	30,000	147·58°	199·02°	270·2°
2,000	97·95°	135·23°	182·9°	32,000	149·28°	201·21°	273·7°
3,000	103·33°	142·17°	192·1°	34,000	150·88°	203·32°	276·0°
4,000	107·27°	147·34°	199·6°	36,000	152·52°	205·40°	278·9°
6,000	113·58°	155·47°	210·8°	38,000	154·11°	207·25°	281·9°
8,000	118·60°	161·95°	219·6°	...	...	...	...
10,000	122·72°	167·31°	226·5°	40,200	155·60°	...	...
12,000	126·81°	171·87°	233·1°	...	Critical	...	...
...	...	...	...	41,240	...	210·5°	...
...	...	...	...	...	...	Critical	...
...	...	...	...	43,500	...	...	287·77°
...	...	...	...	...	...	...	Critical

TABLE OF CONSTANTS

	Absolute boiling- point.	Absolute melting- point.	Absolute critical- point.	Critical pressure (mm.)	Density at boiling- point.	Colour of liquid.
Hydrogen	20	16	35	11,600	0·06	Colourless
Oxygen	90·5	below 50	154	44,080	1·131	Bluish
Nitrogen (chemical)	77·54	60	124	20,930	0·791	Colourless
Nitrogen (atmospheric)	77·50	60	...	...	...	..
Carbon monoxide	83·0	66	137	25,400	...	..
Carbon dioxide	193	...	304	55,000	...	..
Nitric oxide	123·1	...	179?	54,000?	...	..
Nitrous oxide	183·2	170·3	310·0	...	...	..
Methane	108·3	...	191	42,400	0·416	..
Ethane	180	below 120	305	38,100	...	..
Propane	228	...	370	33,440	...	..
Ethylene	169·5	104	282	44,080	0·571	..
Acetylene	190·5	...	308	46,375	...	..
Methyl chloride	249·3	...	416	41,000	...	..
Sulphur dioxide	263	...	428·4	60,000	...	..
Fluorine	186	...	...	...	1·11	Yellowish
Chlorine	239·6	...	...	...	1·507	Colourless
Hydrogen sulphide	211·5	...	373	69,900	...	..
Hydrogen phosphide	188	...	...	...	...	..
Ammonia	234·5	197·5	404	85,900	...	..
Helium	below 20	...	...	...	...	..
Neon	30·40	...	below 65	...	...	..
Argon	86·90	...	155·6	40,200	1·212	..
Krypton	121·33	...	210·5	41,240	2·155	..
Xenon	163·9	...	287·8	43,500	3·52	..



*The critical constants.*—The only difficulty in determining the critical temperature is that of maintaining a constant and definite temperature during the experiment. The methods employed in regulating the temperature are described in the appendix and in the chapter on the liquefaction of gases.

The gas or liquid may be contained in one of the capillary tubes of the compression apparatus, or in a sealed tube. There is no difficulty in condensing gases such as carbonic acid, sulphur dioxide, etc., even without employing liquid air. Observations should be made both with rising and falling temperature.

The temperature obtained by direct observation in this way may differ slightly from the true critical temperature, since the volume occupied by the gas is not the true critical volume. Since, however, as will be pointed out again later, a very small change of pressure at the critical temperature involves a considerable change in volume, the error introduced is exceedingly small.

*The critical pressure* is the most easily determined of the critical constants. The liquid or gas is enclosed in the capillary tube of the compression apparatus, and the tube is heated or cooled, so that part of it is just above the critical temperature and part below it. The pressure is then slowly increased till the critical pressure is reached, when the meniscus between the liquid and the vapour in the tube suddenly disappears. Observations may be made both with rising and with falling pressure. (Altschul, *Zeit. Phys. Chem.* ii. 1893, 577).

If the critical temperature and the vapour pressures corresponding to two or more temperatures are known, the critical pressure may be calculated by the method given on p. 236.

*The critical volume.*—The determination of the critical volume is a matter of considerable difficulty, even when the substance in the liquid state can be brought into contact with mercury. This is only possible in the case of liquids whose critical temperatures lie within a very limited range. The difficulty is considerably increased by the fact that a very small change of temperature about the critical point produces a considerable change in volume.

S. Young (*Phil. Mag.*, 1892, 181) has described a method for the determination of the critical volume in the case of liquids which can be brought into contact with mercury at their critical points. The gas, which is contained under pressure in

the capillary portion of a compression tube, is maintained at a temperature slightly above its critical point, and is allowed to expand by slowly turning the screw of the compressor. Separation of liquid takes place momentarily, owing to adiabatic cooling, and the position of the surface is observed. After repeated trials, the volume is so adjusted that, on lowering the pressure very slightly, the surface of the liquid lies almost at the top of the tube, and its volume can be read off directly.

*The method of Cailletet and Mathias (C. r., 1886, 102, 1202)*

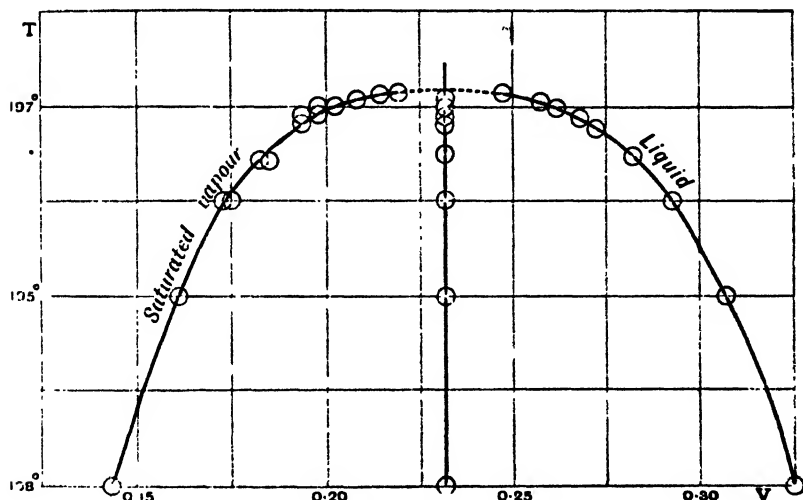


FIG. 115.

certainly yields the most accurate results which have yet been obtained. It has already been pointed out that each of the isothermals for any substance below its critical point contains two points corresponding to the volume occupied by the liquid, and by its vapour under the same pressure. The curve joining these points is tangential to the isothermal corresponding to the critical temperature, *since at this temperature the volumes of the liquid and of the vapour under the same pressure are identical*. According to Cailletet and Mathias, the points representing the mean of the densities of the liquid and of the vapour should lie on a straight line which should also pass through the point corresponding to the critical volume. When  $D_l$  is the density of the liquid, and  $D_v$  the density of the vapour at temperature  $T$ ,

$$\frac{1}{2}(D_l + D_v) = a + bT.$$

The method thus involves the determination of the volumes of the saturated vapour and of the liquid, at temperatures as close as possible to the critical point. The values are plotted in curves, and the curves are continued by hand; the portion of the curve remaining undetermined is shown in the figure by a dotted line. The bisecting line, which is practically straight, is then drawn, and the critical volume is read off on the curve.



FIG. 116.

In order to determine the volumes of the saturated vapour a known quantity of the gas contained in the compression-tube was allowed to evaporate very slowly at constant temperature. When the liquid had completely evaporated the volume of the vapour was observed.

To determine the volumes of the liquid a hydrostatic method was employed. An O-tube (Fig. 116), about 50 cm. long, and 1.5 mm. internal diameter, graduated in millimetres, was sealed to the capillary portion of a compression-tube. The lower portion of the O-tube contained mercury, the upper part and the rest of the apparatus gas.

The O-tube was first slightly cooled so that a few drops of liquid condensed in each limb in order to eliminate the surface-tension effect; the cooling of one limb was stopped, while the condensation was allowed to proceed in the other. The whole apparatus was maintained at constant temperature during each set of readings.

Where  $d$ ,  $d'$ , and  $d''$  are the densities of the liquid, mercury, and vapour, and  $h$  and  $h'$  are the differences in the heights of the mercury and of the liquid columns,

$$hd = h'd' + (h - h')d''.$$

The method of Cailletet and Mathias and the principles which it involves have been thoroughly studied by S. Young (*Chem. Soc. Jour.*, 1897, 446), in the case of the pentane. The following points were investigated:—

1. Whether the law of Cailletet and Mathias holds up to the critical temperatures.
2. Whether at the critical point the densities of liquid and vapour do really become equal.

3. Whether the point at which this takes place corresponds to the apparent critical temperature.

4. Whether the apparent critical temperature depends upon the conditions—rising or falling temperature.

He found that the bisecting line was not quite rectilinear, and that in order to calculate the mean values of the densities it was necessary to employ a formula of the type (*Chem. Soc. Jour.*, 1900, 1140),

$$D_t = a + bt + ct^2.$$

The densities of liquid and vapour appeared to be equal at the critical point.

With regard to the real critical temperature, it was found that when the sealed-tube method was employed, the formation of mist and striae was not confined to the critical temperature, but to a limited range of temperature about  $0.2^\circ$  C. on either side of it. When, however, the measurement was made with the pressure apparatus so arranged that the volume could be adjusted, it was possible to determine the critical point to within  $0.05^\circ$  C., the result agreeing within this limit with that obtained from the volume curve. In neither case did a rising or falling temperature produce a different result.

A method for the determination of the specific volumes of liquids and of their saturated vapours has been described by S. Young (*Chem. Soc. Jour.*, 1891, **59**, 37), and has been employed by him in the case of organic substances, which are liquids at the ordinary temperatures.

The liquid is introduced into a graduated capillary tube, which is subsequently sealed; all the air is removed by boiling the liquid *in vacuo*. It is necessary to determine the volume of the sealed end of the tube at the close of the experiments.

Suppose that the liquid is contained in a tube in contact with its vapour only, and the temperature is raised. The apparent expansion is less than the real expansion for the reason that some of the liquid is vaporised.

If now the upper portion of the tube be kept at constant temperature  $T^\circ$ , and the lower portion at a somewhat lower temperature  $\theta^\circ$ , so that the length of the column of vapour heated to the higher temperature may be varied, we can obtain data which

should be sufficient to enable us to calculate the volumes of the liquid and of the vapour.

Let  $V_r$  be the true volume of the liquid at  $T$ , and  $r$  the ratio of the volumes of the saturated vapour to that of the liquid at the same temperature.

If in the first experiment the whole tube is heated to  $T'$ , and if  $V'_r$  is the apparent volume of the liquid, and  $V'_v$  that of the saturated vapour,

$$(i) \quad V_r = V'_r + \frac{V'_v}{r}.$$

In the second experiment let the lower part of the tube containing  $V_\theta$  volumes of liquid be cooled to  $\theta$ . Let  $V_\lambda$  be the difference between  $V_\theta$  and the volume of the liquid when the apparatus is heated to  $\theta$ , and  $V_n$  the observed expansion.

Then since  $V_\lambda$  volumes of liquid at  $\theta$  fill  $V_\lambda + V_n$  volumes at  $T$ , the total volume of the liquid would, under the same conditions, occupy  $\frac{V_\theta}{V_\lambda} (V_\lambda + V_n)$  volumes. At the same time the expansion has caused some of the saturated vapour to condense; this will be  $\frac{V_\theta}{V_\lambda} \cdot \frac{V_n}{r}$ .

The true volume of the liquid will thus be

$$(ii) \quad V_r = \frac{V_\theta}{V_\lambda} V_\lambda + V_n - \frac{V_\theta}{V_\lambda} \cdot \frac{V_n}{r};$$

two sets of values for  $V_\lambda$ ,  $V_n$ , and  $V_\theta$  must be obtained.

From i. and ii. we have,

$$V_r = \frac{V_\theta (V_r (V_\lambda + V_n) + V_n V'_v)}{V_n V_r + V_r V_\lambda},$$

and for the ratio of the volumes

$$r = \frac{V_\theta}{V_r - V'_r}.$$

If  $S_r$  and  $S_\theta$  are the volumes of one gram of liquid at  $T'$  and at  $\theta$ ,

$$S_r = \frac{V_r \times S_\theta}{V_\theta}.$$

It is, of course, impossible to maintain the conditions so that

consecutive portions of the tube are heated to different temperatures ; there must always be an intermediate portion, one extremity of which is at the higher, and the other at the lower temperature. If this length remains constant during both series of readings in the second experiment, the results are not affected so long as a cylindrical tube is employed.

## CHAPTER XVIII

### SOLUBILITY OF GASES IN LIQUIDS

Historical—Solubility and absorption coefficients—Chemical and physical methods of investigation—Winckler's experiments and results—Estreicher's method.

*Solubility of Gases in Liquids.*—All known liquids, with the exception of mercury, appear to dissolve gases to a greater or less extent. In some cases, however, the quantity absorbed is very small, heavy petroleum oil dissolving only a trace of atmospheric air.

In 1803 Henry discovered the law of absorption of gases, showing that the quantity of gas dissolved by a liquid increased directly as the pressure. In 1807 Dalton developed the law further, proving that the quantity of gas dissolved by a liquid from a mixture depended upon the partial pressure of that particular gas.

In 1855 Bunsen carefully investigated these laws, and found them to hold good in the case of inactive gases over considerable ranges. Like the gas laws, however, they must only be considered as approximating to the truth. Bunsen defined the "coefficient of absorption" of a gas as the volume of it, reduced to standard conditions, which at any temperature, and under normal pressure, dissolved in unit volume of liquid. By means of an interpolation formula with three coefficients,  $\alpha = a + bt + ct^2$ , it was in most cases possible to calculate the absorption coefficient within a range of 20°.

Recent researches have shown that little reliance can be placed upon Bunsen's results.

Winckler (*Ber.*, **22**, 1773) draws the following distinction between the terms coefficient of absorption and solubility:—

That volume of a gas (reduced to 0° and 760 mm.) which

unit volume of a liquid dissolves when the total pressure at the surface of the liquid is 760 mm. is termed the solubility,  $S$ ; that volume which unit volume of a liquid will take up when the pressure of the gas at the surface of the liquid, independent of the vapour pressure,  $p$ , of the liquid, is 760 mm., is termed the coefficient of absorption,  $C$ .

The temperature is taken to be 0° C. in both cases.

$$S = C \frac{760 - p}{760}.$$

The value of  $p$  may differ from the true vapour pressure of the gas in contact with a vacuous space on account of the presence of the gas in the liquid, or for other reasons. The solubility or absorption coefficient is not a direct function of the concentration of the gas in the liquid, since contraction takes place on solution.

In certain cases, in which chemical combination takes place between the gas and the solvent, the laws of Henry and Dalton are not rigidly followed. The quantity of carbon dioxide which water will dissolve does not increase in proportion to the pressure. When, however, carbon bisulphide is used as the solvent the laws are obeyed within the limits of experimental error, and the solubility of the gas decreases with rise of temperature (Woukoloff, *C. r.*, 1889, 674).

The relationship between solubility and temperature and the deviations from Henry's law form part of the great problem involved in the study of mixed liquids. The curves representing the change of solubility with temperature, for gases under constant pressure, appear to indicate that for each gas there exists a point of minimum solubility, and that the temperature corresponding to this point is in some way related to the critical point for the gas.

The problem has been attacked by Van der Waals, Kammerlingh Onnes, Kuenen, and others, and the composition of the liquid and vapour phase, the form of the isothermals, pressure, etc., for several pairs of substances, such as ethylene and carbon dioxide, have been investigated over wide ranges of temperature. Dissimilar substances, such as the permanent gases and water, have not yet been examined; it would be interesting to know more about these phenomena (see p. 225).



The following diagram shows the form of the solubility curve for the commoner gases. In the case of helium (Estreicher),

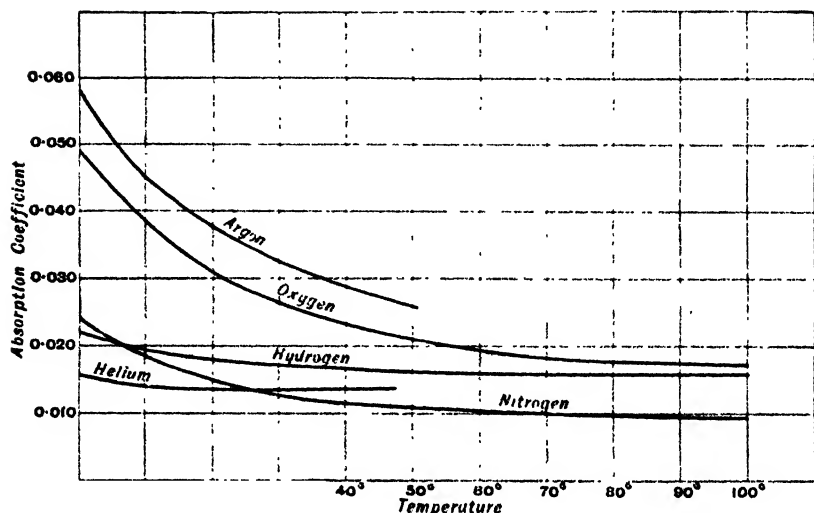


FIG. 117.

and also of hydrogen (Bohr and Bock), the solubility of the gas first decreases with fall of temperature and then increases.

Bohr (*Wied. Ann.*, 1897, **62**, 644) has shown that the relation between the absorption coefficient and the temperatures can be expressed by the equation,

$$C \frac{T}{n} = K,$$

where  $C$  is the absorption coefficient,  $T$  the absolute temperature, and  $n$  and  $K$  are constants dependent on the nature of the gas and liquid. The formula is based upon the theory that the pressure of the gas at the surface of the liquid should be in equilibrium with the osmotic pressure of the gas in solution; the latter would remain constant if the quantity of dissolved gas varied inversely with the absolute temperature. The following results indicate the order of the agreement between experimental results and those re-calculated by means of the formula:—

Temp.	Oxygen (Bohr and Bock, p. 261).	
	Found.	Calculated.
0°	0.0496	0.0493
10	390	386
20	317	317
30	268	269
40	233	234

Winckler (*Zeit. Phys. Chem.*, **9**, 171) has pointed out that the percentage change in the value of the absorption coefficient between 0° + 20° C. is proportional to the cube root of the molecular weight of the gas. This has obviously no direct physical significance.

From the practical standpoint the determination of the solubility of a gas in a liquid presents considerable difficulties. In the first place the temperature of the whole apparatus must be kept constant during the whole experiment, and unless the apparatus can be shaken the time required to establish complete equilibrium between the solution and the gas is considerable. Further, both the gas and the liquid must be absolutely pure, and the volumes and pressures must be accurately measured.

Methods for the determination of the solubility of gases fall under two headings: chemical methods, in which the quantity of a gas dissolved in a liquid under definite conditions of temperature and pressure is estimated by some chemical process, usually by titration with a standard solution; and physical methods, in which the volume of the dissolved gas is accurately measured.

In only a limited number of cases can chemical methods be employed; and as special methods must be applied in every case, the subject cannot be treated generally. In some cases the results obtained by chemical methods serve as a valuable check on the results obtained by physical methods; this is particularly important when, as in the case of oxygen, the results obtained by different experimenters differ considerably.

Winckler (*Ber.*, **22**, 1766) determined the oxygen dissolved in pure water saturated under known conditions of temperature and pressure, by treating the solution with manganous chloride and caustic soda in order to absorb the oxygen, and subsequently titrating the iodine, set free on addition of potassium iodide and hydrochloric acid, by sodium thiosulphate. The values obtained

by this method agreed with those obtained by the volumetric method.

	Chemical method.		Physical method.	
	Winckler.	Winckler.	Bunsen	
Absorption coefficient 0	...	·04890	·04114	
" " 20'	·03103	·03102	·02838	
" " 30'	·02616	·02608	...	

This indicates that Winckler's results are most probably correct.

Since 1891 Winckler has published the results of his investigations with regard to the solubilities of the commoner gases in water. As has already been pointed out, the check afforded by close agreement between the results obtained for oxygen by chemical and by physical methods point to the accuracy of his work.

The glass vessel *a* was filled with distilled water, and the water was made to boil until about one-fifth has evaporated. While the steam was still issuing from the lower end, the tube was plugged by means of a rubber stopper and the apparatus was cooled and weighed in order to determine the weight of the water.

The bulb was placed in a large water thermostat so that only the lower end of the tube projected at the bottom. A second bulb *b* was also placed in the thermostat so that the vertical stems lay close to one another; the second vessel contained only a small quantity of water and was intended to serve as a barometer. The volumes of both vessels had been determined, and the vertical stems were graduated in millimetres.

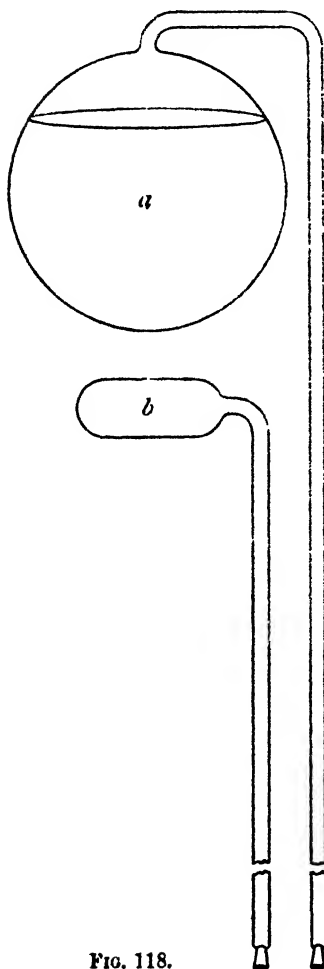


FIG. 118.

The stoppers which closed the lower ends of the vertical tubes were removed below the surface of mercury in a basin, and it was

possible to determine whether the air had been completely removed by comparing the heights of the columns of mercury in the two tubes. It may be pointed out that the weak point of the method lies in the difficulty of completely replacing the whole of the air in the bulbs by steam, and subsequently of determining the pressure of a trace of air by reading the barometric height.

Definite quantities of gas were then introduced into the absorption-bulb and pressure-gauge from a calibrated syphon pipette. The presence of gas in the barometer served to eliminate errors due to the change of vapour pressure of the liquid in presence of the gas; the quantities of gas introduced were such that the pressure was the same in both vessels.

The lower ends of the two vertical tubes were then connected by rubber tubes to two mercury reservoirs; the pressure on the gas was raised to somewhat over atmospheric pressure, and the apparatus was allowed to stand at constant temperature for some hours in order to establish equilibrium between the liquid and the gas. The measurements of pressure and volume were then taken.

The actual method of measurement was as follows: The pressure on the gas in vessel *b* was adjusted so that, whatever might be the temperature, it was practically the same in each experiment. From the observed volume and pressure, and from the volume of the dry gas originally introduced, it was possible to calculate directly the vapour pressure of the solvent. A small correction was applied for the absorption of gas by the water contained in the bulb. The pressure and volume of the gas in the absorption tube was measured at the same time. The pressure on the gas in the latter was corrected for the presence of water vapour, on the assumption that the deviation from the pressure of the vapour in a vacuous space is proportional to the pressure of gas. This assumption appears to be justifiable, since the deviation and range of pressure are both small. At temperatures above 50° the deviation amounted to a few millimetres, and consequently, if it were not corrected for, it would produce a considerable error in the calculation of the absorption coefficient.

The following results were obtained:—

Oxygen (*Ber.*, 1891, 3609).

The coefficients are stated for *every degree* between 0° and 100°; only alternate values between 0° and 34° are given here.

0° C.	0.04890	18° C.	0.03220
2	4633	20	3102
4	4397	22	2988
6	4181	24	2881
8	3983	26	2783
10	3802	28	2691
12	3637	30	2608
14	3486	32	2537
16	3347	34	2471

Nitrogen (*Ber.*, 1891, 3606).

The values are also given between 0 and 100°

0° C.	0.02348	18° C.	0.01594
2	2236	20	1542
4	2130	22	1496
6	2032	24	1452
8	1941	26	1411
10	1857	28	1374
12	1782	30	1340
14	1714	32	1304
16	1651	34	1270

Hydrogen (*Ber.*, 1891, 99).

0° C.	0.02148	18° C.	0.01844
2	2105	20	1819
4	2064	22	1792
6	2025	24	1766
8	1989	26	1744
10	1955	28	1720
12	1925	30	1699
14	1897	32	1685
16	1869	34	1672

Carbon monoxide (*Zeit. Phys. Chem.*, 9, 173).

Measurements are given between 0° and 60°.

0° C.	0.03537	20° C.	0.02319
5	3149	25	2141
10	2816	30	1998
15	2543		

Bohr and Bock (*Wied. Ann.*, 1891, 44, 316) have also determined the co-efficients for the commoner gases by a method similar to that employed by Winckler: the results differ some-

what from those already stated. They obtained the following values for the absorption coefficient, which are stated in the original paper for every degree between 0° and 100° C.:—

Oxygen.

0° C.	0.04961	16° C.	0.03425
2	4720	18	3292
4	4496	20	3171
6	4286	22	3059
8	4089	24	2954
10	3903	26	2855
12	3732	28	2762
14	3573	30	2676

Hydrogen.

0° C.	0.0203	40° C.	0.0152
4	198	50	146
8	192	60	144
12	187	70	146
16	182	80	149
20	177	90	155
30	163	100	166

Estreicher (*Zeit. Phys. Chem.*, 1899, **31**, 176) has described a simple apparatus for the determination of solubilities of gases in liquids. The liquid partially fills a globe of known capacity which is exhausted and weighed. The globe is sealed to a spiral tube of capillary dimensions, which connects it with a burette containing the gas so that the globe can be shaken. After exhausting the connecting-tube, the gas is admitted to the globe, and the absorption is determined by measuring the decrease in the volume of the gas and from the known capacities of the globe and connecting-tubes. The whole apparatus is contained in an Ostwald thermostat. He determined the solubilities of argon and helium by means of it.

## CHAPTER XIX

### SPECIFIC HEATS

General principles—Experiments of Déclaroche and Berard—Experiments and results of Regnault and E. Wiedemann—Witkowski's investigation of the specific heats of gases at low temperatures—The specific heats of gases at constant volume—Joly's experiments—The ratio of the specific heats.

THE specific heat of a substance is defined as the quantity of heat required to raise the temperature of unit mass of it one degree. In the case of gases, however, this quantity varies according as the heating takes place at constant pressure, or at constant volume.

The determination of the specific heat of a gas at constant pressure is theoretically simple. The gas, heated to a definite temperature, is passed in a continuous stream through a spiral tube immersed in the water of a calorimeter. The specific heat is calculated from the mass of the gas, from the thermal capacity of the calorimeter, and from the rise of temperature during the experiment, or in some cases by regulating the conditions until the heat supplied to the calorimeter by the gas exactly compensates for the heat lost by radiation and conduction. The latter method possesses the advantage that, since the fall of temperature in the gas does not vary throughout the experiment, variations of its specific heat with temperatures need not be taken into consideration.

So far no successful attempt has been made to determine the specific heat of gases by measuring the rise of temperature produced when heat is supplied to them. A method similar to that employed by Callendar (*Brit. Assoc.* 1899) in determining the specific heat of water, might be applied to gases with a view to determining the specific heat with very small quantities. It

might be possible to circulate the gas through the apparatus by means of the arrangement described on p. 101, and to measure the rate of flow of the gas by passing it through a tube containing water maintained at a constant temperature, and then through weighed tubes containing an absorbent for water. The vapour pressure of the water, the pressure on the gas, and the increase of weight in the tubes, would give the rate of flow of the gas.

The first attempts to determine the specific heats of gases by Laplace and Lavoisier, Dalton, Gay-Lussac, and others were, for the most part, indirect, and based upon theoretical notions with regard to the gaseous state. In 1813 Délaroché and Bérard determined the thermal capacities of a number of gases by passing a current of the gas, heated to a known temperature, through a coil immersed in a calorimeter.

The gas was contained in a bladder (Fig. 119), which was attached to a tube leading to the heating apparatus and coil. The bladder was enclosed in a glass vessel, which was connected with a small gasholder, so that air could be forced between the bladder and the walls of the vessel, increasing the pressure on the gas contained in the bladder. The gas from the bladder passed through a tube surrounded with steam, then through a glass tube containing a thermometer, through the coil immersed in the calorimeter, and was received in a second bladder similar to the first. By an arrangement of taps and tubes the gas could be made to pass from the second bladder to the first, following the same course through the heating apparatus and calorimeter.

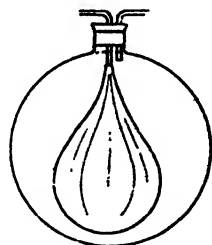


FIG. 119.

The specific heat of the gas, with regard to air in one set of experiments, was calculated from the temperature at which the heat supplied by the gas and by conduction became equal to the heat lost by radiation.

In a second set of experiments the calorimeter was cooled to  $2^{\circ}$  below the temperature of its surroundings, and a current of gas was passed through the coil till the temperature had risen  $4^{\circ}$ . The weight of any gas required to produce this effect bore the same relationship to the weight of air required to produce the same rise of temperature, as the specific heat of the gas to the



specific heat of air. The absolute specific heat of air was also determined.

The experiments were conducted with the greatest care, but probably, owing to the difficulty of determining with accuracy the quantity of gas employed, the results are of little value. The result obtained for the specific heat of air between 30 and 100 is more than 10 per cent higher than that obtained by Regnault. Further, this result indicated that the specific heat of air increased rapidly with rise of temperature, and that although it increased with rise of density, it did not do so in like proportions. Both these conclusions were shown by Regnault to be false.

The results obtained by Regnault for the specific heats of air and the commoner gases are probably the most accurate that have yet been published. His researches, carried out in the early forties, are described in volume xxi. of the *Mémoires de l'Académie*; the principal results are stated in a paper in the *Comptes rendus* (1853, 36, 676).

The gas to be examined was compressed into a stout copper vessel holding 30 litres: the temperature of the vessel was maintained at 0°, and the volume of gas was deduced from the initial and final pressures, which ranged from 9 to 3 metres of mercury. The gas escaping from the reservoir through a valve, regulated by means of a micrometer screw *a*, entered a platinum spiral *b* 8 cm. in diameter, and 10 metres long, maintained at a constant and definite temperature. In order to maintain a constant current of gas, a mercury or water manometer *c* was interposed between the valve and the coil; the pressure in the manometer was kept constant during each experiment.

The end of the long platinum coil, which was usually heated in an oil-bath, passed out through the side of the jacket on which it was enclosed and entered the side of the calorimeter. The connection was made by means of a piece of glass tube imbedded in cork, in order to reduce to a minimum the quantity of heat entering the calorimeter by conduction. The calorimeter *d* consisted of four flat brass boxes placed one above the other, and divided internally by spiral strips, so that the gas was compelled to pass from the middle of one box to the outside of the next, and *vice versa*.

Separate experiments were performed to determine whether the temperatures at which the gas left the spiral and the calori-

meter differed appreciably from the temperatures of the spiral and calorimeters themselves.

In order to determine the specific heats of gases under pressure, the gas which escaped from the calorimeter passed into

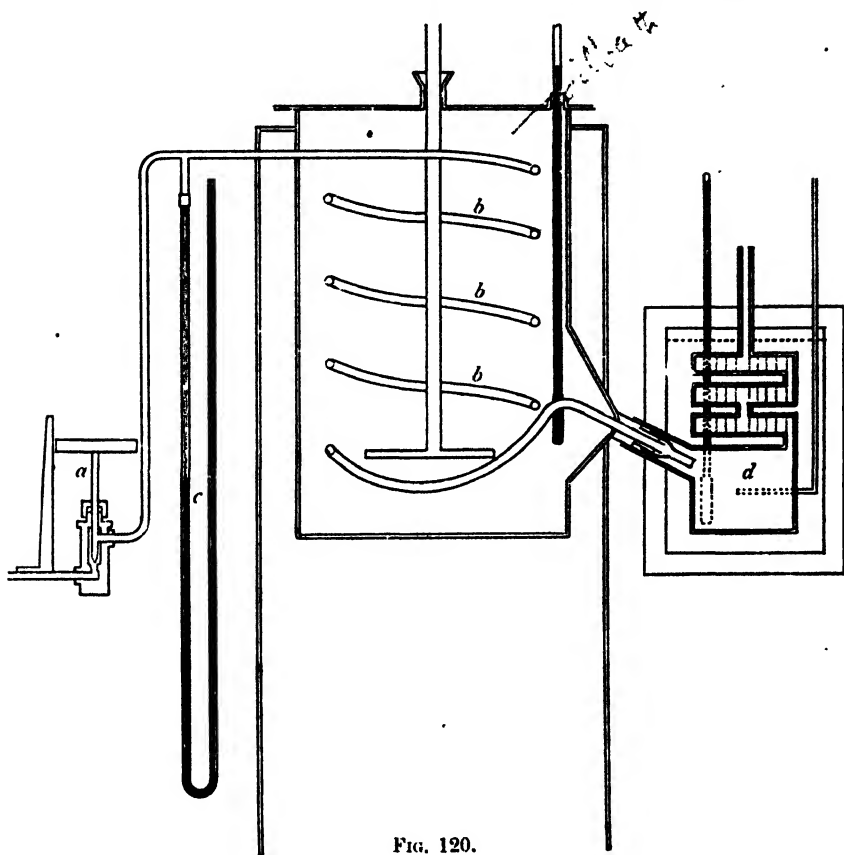


FIG. 120.

a tube connected with a manometer and valve by which the pressure might be regulated.

In calculating the result, the volume of gas was obtained from the initial and final pressures in the reservoir, taking into consideration the deviations from Boyle's law as already determined (p. 162). The mass of the gas was obtained by dividing the volume by the density determined experimentally (p. 125). The errors in Regnault's density determinations only amount to one part in four thousand, and do not appreciably affect the final result.

When the gas was not passing through the calorimeter, the latter continued to gain heat from three sources :—

(i) By convection; this was practically proportional to the  $(T - \theta)$ , the difference of temperature between the calorimeter and the coil.

(ii) By radiation.

(iii) By conduction.

(ii and iii) have practically a constant value, which may be represented by a rise of temperature of  $k$  in unit time.

The rise of temperature in the calorimeter was observed for ten minutes before the gas was admitted. Expressing the rise of temperature per minute by  $\Delta\theta$ ,

$$1. \quad \Delta\theta = A(T_0 - \theta_0) + k,$$

where  $A$  is a constant.

The gas was then admitted to the apparatus, and readings of the temperature of the calorimeter and of the heating-bath were taken at the end of each minute. When the current of gas was stopped the change of temperature of the calorimeter was again observed for ten consecutive minutes.

$$(2) \quad \Delta\theta_1 = A(T_1 - \theta_1) + k.$$

The values of  $A$  and  $k$  can be determined from those two equations, and applied to the calculation of the total disturbance during the equation.

$$\Delta\theta + \Delta\theta' + \text{etc.} = A(T + T' + \dots T^n - \theta - \theta' - \dots \theta^n) + nk = r.$$

This value must be subtracted from the total rise of temperature in the calorimeter, in order to calculate the heat conveyed to it by the gas alone. If  $T$  is the temperature of the coil, since the temperature of the calorimeter rises steadily from  $\theta$  to  $\theta^n$ , the heat lost by the gas is expressed by

$$WC_p \left[ T - \frac{(\theta + \theta^n)}{2} \right],$$

and the heat gained by the calorimeter

$$C(\theta^n - \theta - r),$$

where  $W$  is the mass of the gas and  $C_p$  its specific heat, and  $C$  is the thermal capacity of the calorimeter.

The following results were obtained for the commoner gases—

Oxygen . . . . .	0·2182	Nitrous oxide . . . . .	0·2238
Nitrogen (atmospheric)	0·2440	Nitric oxide . . . . .	0·2315
Hydrogen . . . . .	3·4046	Carbon monoxide . . . . .	0·2479
Carbon dioxide . . . . .	0·2164	Ammonia . . . . .	0·5080

The probable accuracy of Regnault's results are indicated by the exactitude of the results of his investigation of the effect of temperature and pressure on the specific heat.

In the case of air the specific heat was found to be constant.

Temperature.	Specific Heat of Air.
- 30° to + 10°	0·2377
+ 10° „ 100°	0·2379
+ 100° „ 225°	0·2376

In the case of carbon dioxide the specific heat varied with the temperature.

Temperature.	Specific Heat of Carbon Dioxide.
- 30° to + 10°	0·18427
+ 10° „ + 210°	0·21692

The results obtained for the thermal capacities of air over wide ranges of pressure are equally accurate.

E. Wiedemann (*Pogg. Ann.*, 1876, **157**, 1) has also determined the specific heats of a number of gases chiefly with a view to investigating the relationship between specific heat and temperature. The results agree fairly closely with those obtained by Regnault, but there is no reason for assuming that they are more accurate; the differences occurring in individual sets of experiments appear to be of the same order.

#### SPECIFIC HEAT OF AIR

	Highest.	Lowest.	Mean.
Regnault . . . . .	0·2389	0·2354	0·2374
Wiedemann . . . . .	0·2414	0·2374	0·2389

\* The gas was heated in passing through a copper cylinder filled with copper turnings and enclosed in an oil-bath; the calorimeter consisted of three small cylinders connected in series and contained in a vessel filled with water. The quantity of

water in the calorimeter was only one-tenth of the quantity employed by Regnault.

The gas was contained in a rubber balloon holding 20 litres, which was enclosed in a large glass jar after the manner of Delaroche and Bérard. The jar was connected with a gasholder standing on a weigh-bridge capable of indicating a difference of 5 grams. The whole arrangement is decidedly weak, but although errors might have been introduced through inaccurate determinations of volume, and diffusion of gases like ammonia and carbon compounds through the rubber, the total discrepancy cannot in all cases be accounted for in this way. Further, if the gas diffused through the rubber the result would be too low; in the case of carbon dioxide and air the reverse is found to be the case.

The character of the difference varies in the case of different gases, as will be seen in the following table:—

	Air.	Hydrogen.	Carbon Dioxide.	Carbon Monoxide.
Regnault	0.2375	3.410	0.2024 (10 - 100)	0.2479
Wiedemann	0.2389	3.405	0.2088 (15 - 93)	0.2426
$\Delta$	+0.0014	-0.005	+0.0064	-0.0053
$\Delta$ per cent	+0.6	-0.153	+3.0	-2.0

The irregularity of the differences would preclude the possibility of the errors being due to inaccuracies in the determination of the thermal capacity of the calorimeter.

In the case of air and hydrogen, gases in which the specific heat does not vary with temperature, the differences are small. The discrepancies in the case of carbon monoxide and dioxide are, however, considerable, and it is possible that the error may be due to the fact that the methods of calculation which were employed did not express with sufficient accuracy the loss of heat sustained by the gas in raising the temperature of the calorimeter.

Wiedemann attributes the difference in the case of air to inaccurate determinations of temperature on the part of Regnault. In the face of the close agreement between the results obtained

for the specific heat of air at different temperatures by the latter this is hardly possible. It is probable that Regnault's result for the specific heat of air is the more accurate.

The recent determination of the specific heat of air at constant pressure by Witkowski (*Phil. Mag.*, 1896, **42**, 1) tend to confirm the results obtained by Regnault. His method differed little from that of the latter, but his experiments were conducted over a range of temperature between  $+98^{\circ}$  and  $-170^{\circ}$  C.; liquid oxygen and ethylene were used as refrigerants. The air was compressed into small metal cylinders which were weighed before and after each operation; as much as 40 grams of air was used in some of the experiments. This method eliminates the error involved in correcting for the compressibility of the gas and for the expansion of the vessel in which it is inclosed.

In order to determine the temperature of the gas at the point at which it entered the calorimeter a thermo-electric junction was employed. The wire was surrounded by a metal tube in contact with the gas, and through which a current of air from an independent source was circulated. The temperature of the calorimeter was determined by means of a mercury thermometer, and the temperature of the heating or cooling chamber containing the coil by means of a hydrogen thermometer.

In making an observation the temperatures of the calorimeter and of the coil were determined during each minute of the experiment. After ten minutes from the commencement, the cock of the cylinder containing the air was opened, and the air was allowed to flow at a constant rate through the apparatus; its temperature was determined at the end of each minute. When the cylinder was empty the cock was closed, and readings of the temperature of the calorimeter and of the coil were again taken during the succeeding ten minutes.

With the aid of the determinations of the temperatures of the coil and of the calorimeter a curve was drawn showing the variations of the temperature of the latter. The curve consists of three nearly linear portions; the mean slope of the first and last portions, representing the heating or cooling effect while the air was not passing, was taken as indicating the external heating or cooling effect during the principal period of the experiment.

The results obtained at atmospheric pressure are as follows:—

---

Between + 98° and + 20°	.	.	0.2372
" - 77° " + 16°	.	.	0.2374
" - 102° " + 17°	.	.	0.2372
" - 170° " + 18°	.	.	0.2427
Regnault obtained the value	.	.	0.2374

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Whether the increase of the specific heat at  $-170$  is due to change of temperature alone remains undetermined. It is probable that it may in some degree be due to variations in the pressure, which should have a considerable influence at low temperatures.

It still remains to determine the specific heats of gases like carbon dioxide, which vary considerably over small ranges of temperature. It is obvious that the method employed should be one in which a current of the gas is heated or cooled through a definite range of temperature, in order to eliminate errors which may be introduced through the gradual increase of temperature of the calorimeter, and which cannot be corrected for with certainty.

✓ THE SPECIFIC HEAT AT CONSTANT VOLUME.—The specific heats of gases at constant volume have been experimentally determined by Joly (*Phil. Trans.*, 1891, 73; 1894, 943, 961). Joly's method involved the use of the steam calorimeter in which the heat capacity of a substance is determined in terms of the latent heat of steam, by measuring the amount of water condensed on its surface.

Two globes, spun from one piece of gun-metal and closed by means of screw-down cocks, were suspended inside a steam-chamber by wires connected with the pans of a balance. The steam-chamber was jacketed so that the initial temperature of the globes could be accurately controlled. Each globe was provided with a catch-water or inverted cone of platinum suspended below it to receive the water produced by condensation of the steam. The suspending wires were surrounded, at the points at which they passed outside the steam-chamber, by coils of platinum wire heated by means of an electric current.

The masses and dimensions of the globes were first so adjusted that when steam was admitted to the chamber the same quantity of water was condensed upon each of them, indicating that the total heat gained was the same in each case, and that errors due to radiation and conduction were eliminated.

One of the globes was then filled with gas under known conditions of temperature and pressure, and both were replaced in the chamber and balanced one against the other. Steam was then admitted, and weights were placed on one of the pans of the balance to compensate for the excess of water condensed on the globe containing the gas.

If  $\theta_1$  and  $\theta_2$  are the initial and final temperatures of the globe,  $L$  the latent heat of steam, and  $W$  is the weight of water condensed in raising the temperature of  $g$  grams of the gas from  $\theta_1$  to  $\theta_2$ , and  $C$  the specific heat of the gas,

$$Cg(\theta_2 - \theta_1) = WL,$$

supposing that no change takes place in the volume of the globes. It was, however, found necessary to apply corrections for the slight difference in the thermal capacities of the globes; for their thermal expansion and dilation under pressure; and for the change of buoyancy produced by expansion. The slight errors due to the thermal effect produced by expansion and to leakage could be neglected.

THE RATIO OF THE SPECIFIC HEATS.—Within the limits of Boyle's law the ratio of the specific heats at constant pressure and at constant volume should have a definite value for each gas.

The ratio of the specific heats was first determined by Clément and Désormes in 1819 in the following manner. A globe fitted with a large stopcock was in communication with a water manometer and an air-pump. The globe was exhausted so that the water rose a few centimetres in the manometer, the air-pump was disconnected, and the tap was opened for a moment and closed again. When the tap was opened air entered, and the air already in the globe was compressed, with consequent rise of temperature.

If  $B$  is the barometric pressure and  $(B - p_1)$  the initial pressure in the globe, on opening the stopcock  $V_1$  volumes of gas are compressed to  $V_2$  volumes where

$$(1) \quad (B - p_1)V_1^k = BV_2^k,$$

the process being adiabatic (p. 185).

• On cooling the pressure becomes  $(B - p_2)$ , and since the volume of the gas in the globe is scarcely altered by the change in the position of the liquid in the manometer,

$$(2) \quad (B - p_2)V_2 = (B - p_1)V_1.$$



Combining equations (1) and (2),

$$k = \frac{\log B - \log (B - p_1)}{\log (B - p_2) - \log (B - p_1)}$$

For small differences of pressure,

$$k = \frac{p_2}{p_1}$$

The originators of the method obtained the number 1.354 for air; the true value for the ratio is probably 1.405, the value for the constant obtained by Röntgen by this method (*Pogg. Ann.*, 1873, 206).

The difficulty of obtaining good results by this method lies in the fact that, on account of the great difference between the thermal capacities of the gas and of the walls of the glass globe, the outer layers become cooled immediately, and the value of  $p$  is always low. It has, however, been applied in a modified form by Röntgen to the determination of the ratio for air.

Although the method of Kundt and Warburg for determining the ratio of specific heats from the velocity of sound in the gas gives excellent results, it is based upon the supposition that the velocity of sound is a direct function of the ratio of the specific heats. This is highly probable; but as important theoretical conclusions are based upon the value of the ratio in the case of the so-called monatomic gases it will have to be investigated.

Callendar has employed the platinum resistance thermometer to measure the actual temperature of the gas. The platinum wire is made very short, and a compensating arrangement is introduced to eliminate heating effects in the leads.

The method of Kundt and Warburg is that usually employed in determining the ratio of the specific heats of a gas.

The velocity of a sound in a gas is expressed by the equation

$$u = \sqrt{\frac{v^2}{m} \left( \frac{dp}{dv} \right) k}$$

where  $v$  is the volume occupied by mass  $m$  under a pressure  $p$ , and  $k$  is the ratio of the specific heats.

Now since within the limits of Boyle's law  $v \frac{dp}{dv}$  is a constant for all gases, and  $\frac{v}{m}$  may be expressed by  $\frac{T}{d}$ , where  $d$  is the

density of the gas under normal pressure, and at the absolute temperature  $T$ , the relative velocity of sound in two gases is given by the equation

$$\frac{u}{u'} = \sqrt{\frac{d'kT}{dk'T'}}$$

The relative wave-lengths of sound of the same pitch in the two gases may be obtained by substituting  $\lambda$  for  $u$  in the preceding equation

$$\frac{\lambda}{\lambda'} = \sqrt{\frac{d'kT}{dk'T'}}$$

The apparatus employed by Kundt and Warburg is shown in Fig. 121. The tube A is about 60 cm. in length, and has an internal diameter of about 7 mm. The rod B passes through the closed end of the outer tube so that it projects for the same distance on each side of the junction; it may be sealed into position or fixed by means of a piece of rubber tube. The end

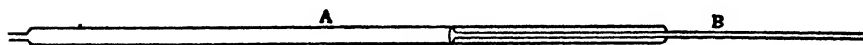


FIG. 121.

of the rod which lies inside the tube should be somewhat flattened. The rod should be 7 mm. in diameter, and the walls of the tube 1.5 mm. thick.

The tube is made narrow at the open end and is connected both to the pump and to the apparatus for introducing the gas. The connection is usually made by means of a piece of rubber tube which can be closed by a screw clip *so as to produce an echo*. If it is necessary to seal the whole apparatus together the echo may be produced by placing a piece of glass rod about 2 cm. long, and of nearly the same diameter as the tube, inside the tube; this can be moved about till the best result is obtained.

When the rod is rubbed the longitudinal vibrations set up in it are transmitted to the gas, and in order to record the positions of the nodes and antinodes, the positions of maximum and minimum disturbance, a small quantity of light powder is placed in the tube. The powder gathers in little heaps along the length of the tube; the distance between two consecutive heaps is one-half wave-length.

Lycopodium powder may be used for inactive gases; it must

be previously<sup>\*</sup> dried in a desiccator and the tube must be very thoroughly cleaned and dried before it can be introduced. • For chemically active gases precipitated quartz may be used; precipitated silica containing a little sodium chloride which had been fritted in the blowpipe flame and subsequently ground in an agate mortar was found to give better results.

After introducing the gas and closing the rubber tube, the tube is tapped with a knife so that the powder lies in a line along the bottom. The tube is then turned slightly on one side and held firmly, while a piece of cotton wool, dipped in alcohol and squeezed dry, is drawn firmly along the rod. The operation is repeated until a satisfactory series of readings can be obtained.

The value of  $\lambda$  is usually obtained by reading off the positions of the three extreme heaps of powder at each end of the tube and counting off the intermediate ones. The readings are taken by reference to a silvered glass scale placed below the tube.

In dealing with a gas of the density of air no difficulty is experienced, but with light gases such as helium or neon it is not easy to obtain good results. In the case of helium, at least six tubes were tried before one was found with which readings could be obtained. The difficulty lies in the small mass of the gas which is incapable of moving the particles of powder. Waves appear to be formed, but they are propagated through the glass and not through the gas; "glass-waves" may be recognised by the spiral appearance of the dust-heaps to which they give rise.

After determining the wave-length of sound in the gas, air is introduced, and the experiment is repeated. The two results are strictly comparable, as the fundamental note given by the glass rod is independent of external conditions. The value of the ratio of the specific heats for air has been found by Röntgen to be 1.405; its probable value is 1.408, that obtained from the velocity of sound in air, the mean of the best determinations.

The temperature may be determined by means of a thermometer placed beside the tube on the glass scale, or the tube may be enclosed in a water-jacket.

If it is intended to determine the absolute velocity of sound in the gas from the vibration frequency of the glass rod and the wave-lengths, it is necessary to apply a correction for the retard-

ation produced by the tube. Kirchhoff (*Pogg. Ann.*, 1868) gives the following formula for the correction,

$$u = v \left( 1 - \frac{a}{v \sqrt{\mu}} \right),$$

where  $v$  is the velocity of sound through a large space, and  $a$  is a constant, a function of the viscosity and conductivity for heat of the gas.

Webster Low (*Wied. Ann.*, 1894, 682) has verified this equation in the case of air. The correction is small, and would nearly disappear in determining the velocity of sound in one gas by comparison with another.

*The limiting values of the ratio  $\frac{C_p}{C_v}$ .*

For a perfect gas the translational energy of the molecules may be expressed by  $\frac{1}{2} mn\bar{u}^2$ , where  $m$  is the mass of a molecule,  $n$  the number of molecules in unit volume, and  $\bar{u}$  their mean velocity; and if the temperature be raised through one degree the change in kinetic energy of the molecules may be expressed by  $mn\bar{u}^2$ .

$2T$ .

If  $C_v$  is the specific heat at constant volume,

$$(1) \quad C_v = \left( \frac{1}{2} \bar{u}^2 + E \right),$$

where  $E$  is the energy absorbed in doing internal work.

By employing the thermodynamic cycle on p. 185, it was found that

$$(2) \quad C_p - C_v = \frac{p}{T}.$$

The number of impacts of a molecule moving with mean velocity  $\bar{u}$  on the walls of a cubical vessel of unit volume will be  $\frac{\bar{u}}{2}$  per second, and since the impulse is represented by  $2 m\bar{u}$ , and since the total pressure is equal to the product of the two,

$$\text{total pressure} = m\bar{u}^2;$$

or since one-third of the molecules may be supposed to move in a direction parallel to each axis of symmetry,

$$p = \frac{1}{3} m\bar{u}^2,$$

where  $p$  is the pressure on unit area; and if we consider the volume of unit mass,

$$pv = \frac{u^2}{3}.$$

Substituting the value of  $pv$  in equation (2),

$$(3) \quad C_p - C_v = \frac{u^2}{3T}.$$

$$(4) \quad C_v = \frac{u^2}{2T} + \frac{u^2}{3T} + E.$$

$$= \frac{5}{6} \frac{u^2}{T} + E.$$

From (1) and (4),

$$\frac{C_p}{C_v} = \frac{\frac{5}{6} \frac{u^2}{T} + E}{\frac{1}{2} \frac{u^2}{T} + E}.$$

For a monatomic gas within the limits of the simple gas-equation  $E = 0$ , hence

$$\frac{C_p}{C_v} = \frac{5}{3} = 1.667.$$

For a polyatomic gas the value of  $E$  becomes considerable, and the value of the ratio approaches 1. For a diatomic gas its value should be 1.400.

These limiting values have been assigned to the ratio within the limits of the gas-equation only, and cannot be extended to highly compressed gases. Capstick (*Phil. Trans.*, 1895, 186A, 572) and Ramsay, Perman, and Rose-Innes (*Phil. Trans.*, 1897, 189, 167) have investigated a number of complex substances, and the latter have formed values for the ratio in the case of either as high as six units. Witkowski (*Phil. Mag.*, 1896, 42, 1) and Messrs. Baly and Donnan measured the velocity of sound in the commoner gases and found that the value of the ratio suffered but little variation over wide ranges of temperature.

Love (*Phil. Mag.*, July 1899) has pointed to an interesting connection between the value of the ratio for the perfect gas and the Joule-Thomson effect, the latter expressing the deviation from the simple gas law. Taking the value for a perfect diatomic gas

to be 1·400, he calculates that under normal conditions its value for air should be 1·403: this is probably close to its true value.

TABLE

	<i>k.</i>		<i>k.</i>
Air	1·4053 (Rontgen)	Hydrogen	1·414
„	1·4053 (Wulner)	Nitric oxide	1·404
„	1·4106 (Kaysir)	Carbon monoxide	1·411
„	1·41 (Jamin and Richard)	Carbon dioxide	1·264
Oxygen	1·408	Methane	1·269
Nitrogen	1·414	Argon, Helium, etc.	1·66

## CHAPTER XX

### EFFUSION, TRANSPIRATION, AND DIFFUSION

THE study of the phenomena which are grouped together in this chapter involves a considerable knowledge of mathematical physics. A complete account of the more important theoretical and experimental investigations connected with them will be found in O. E. Meyer's work on the *Kinetic Theory of Gases*. I have only treated the subject superficially.

The rate of effusion of gases has recently been made the subject of an investigation by F. G. Donnan: the following is a short abstract of his memoir (*Phil. Mag.*, 1900).

It was first observed by Leslie in 1804 that rate of flow of a gas through a small aperture was connected with its density. In 1820 C. G. Schmidt deduced from his experiments the law, which was afterwards, in 1846, rediscovered by Graham, that the rate of efflux was inversely proportional to the square root of the density of the gas. Taking the time required for the passage of a certain volume of the gas,

$$\frac{t_1}{t_2} = \sqrt{\frac{\rho_1}{\rho_2}},$$

where  $\rho$  is the density of the gas.

In 1839 Saint-Venant and Wantzel proved experimentally that the efflux was independent of the external pressure: this phenomenon was subsequently rediscovered by Graham, Hirn, Napier (1867), and Wilde (1886). The latter obtained an equation expressing the adiabatic efflux of the gas based on the assumption that the pressure at the *vena contracta* is equal to the external pressure; and observed that this equation leads to an absurdity when the external pressure is zero.

Graham's experiments showed that when the diameter of the hole was sufficiently great with regard to the thickness of the septum in which it was pierced, viscosity effects could be neglected. That hydrogen did not conform so exactly to the law as did the other gases, he attributed to the fact that the viscosity effect was more marked owing to the lightness of the gas. In 1857 Bunsen (*Gasometrische Methoden*) applied the method of effusion to the determination of gas densities by measuring the time required for a certain volume of gas to escape from a cylindrical vessel through a hole in a platinum plate at the top. The gas was confined under pressure over water or mercury, and the change of volume was determined by means of a float inside the cylinder. The method could be applied to the determination of the densities of simple gases or of mixtures, for since the phenomenon is independent of molecular motion there is no separation of gases at the jet.

The general theory of the adiabatic efflux of a perfect gas has more recently been studied by Hugoniot and Osborne Reynolds on the one hand, and by Parenty on the other. In both cases the following assumptions are made:—

- (1) That viscosity effects are eliminated.
- (2) That the ideal gas laws hold.
- (3) That the efflux is adiabatic.
- (4) That the motion is steady.

From their results Dr. Donnan has deduced formulæ representing the relative periods required for the efflux of the same volume of two gases in terms of their densities  $\rho$ , and of their values of  $k$ , the ratio of the specific heats.

$$\frac{t_1}{t_2} = \frac{f(k_2)}{f(k_1)} \sqrt{\frac{\rho_1}{\rho_2}}.$$

In the Hugoniot-Reynolds formula

$$f(k) = \left[ \left( \frac{2}{k-1} \right)^{\frac{k+1}{2(k-2)}} \right] k^{\frac{1}{2}};$$

in the Parenty formula

$$f(k) = 1 - \left( \frac{2}{k+1} \right)^{\frac{1}{k-1}}.$$

In comparing the rates of effusion of a monatomic and of



a diatomic gas, such as air and argon, for which the values of  $k$  are 1.408 and 1.67 respectively,

$$\frac{t_1}{t_2} = 1.06 \sqrt{\frac{\rho_1}{\rho_2}} \text{ (Hugoniot-Reynolds),}$$

or,

$$\frac{t_1}{t_2} = 1.08 \sqrt{\frac{\rho_1}{\rho_2}} \text{ (Parenty):}$$

expressions which differ considerably from the simple isothermal formula already given. The Hugoniot-Reynolds formula appeared to be the more correct.

To return to the experimental side of the question. In 1897 Ramsay and Collie showed that though the rate of flow of the commoner gases through a porous plug into a vacuum appeared normal, argon and helium gave considerably higher velocities; Donnan continued the investigation to determine whether the irregularities could be accounted for in the manner that has already been indicated.

*Method of measurement and description of apparatus.*

It will be seen that the theory sketched in the foregoing section only leads to simple comparison-formulae for the case of effusion in which the back-pressure is small in comparison with the pressure in the gas-reservoir. The following experiments were made with an initial pressure in the gas-reservoir which was about 700 mm. in one series and about 500 mm. in the others, the back-pressure rising from zero to 60 and 47.5 mm. respectively. The principal condition was, however, that the apparatus should be such as to admit of measurements being made with small quantities (20-30 c.c.) of the rarer gases. It was necessary, therefore, to employ very small apertures in order to reduce the unavoidable error in the time-measurement<sup>1</sup> to a sufficiently small percentage. There was a limit placed to the thickness of the partition, seeing that it had to withstand pressures approaching that of an atmosphere without collapsing, and so the conditions imposed tended rather in the direction of viscosity-effects. As will be seen in the sequel, such effects made themselves apparent. They could doubtless have been avoided by the employment of large quantities of gas and much larger apertures, but that was not possible in the present case. The apparatus

<sup>1</sup> The time was measured by a stop-watch marking fifths of a second.

employed is shown in Fig. 112: *a* is the gas-reservoir, the gas being introduced through the capillary tubing *b c d* by means of the gas-syphon *e*. The pressure was read off in the closed barometer-gauge *f* by means of a mirror-glass scale. The effusion-plug, or partition containing the effusion-aperture, was placed at or near the lower extremity of the glass tube *g*; *h* represents a ground-glass joint with external mercury seal. During an experiment, the taps *i*, *j*, *k*, and *l* being closed and *m* open, the gas passed from the reservoir *a* into the vacuous receiver *p* through the narrow aperture in the effusion-plug. The tube *n* led to a Töpler-pump, which served to evacuate the apparatus and to collect the gas again at the conclusion of an experiment. Both gas-reservoir and receiver were kept at a constant temperature by being immersed in a very large beaker of water.

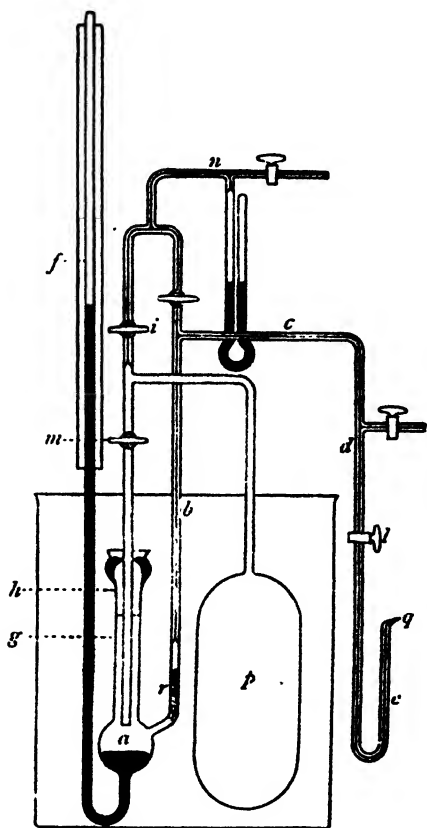


FIG. 122.

The temperature of the water was maintained uniform and constant by means of a stirrer with horizontal screw-shaped blades driven by a Henrici hot-air motor, and an Ostwald temperature-regulator filled with toluene.

In order to make a measurement with the apparatus, the mode of procedure was as follows:—The end *q* of the bent capillary tube was drawn off to a fine point and sealed. The taps *i*, *j*, *l*, and *m* were opened and the apparatus exhausted. These taps were then closed, and the tube containing the gas over mercury brought over the sealed point *q* by raising and lowering the mercury-trough. The drawn-out end, which had been previously weakened by a file scratch, was now broken by

pressing the top of the tube against it, and the gas admitted to the reservoir by opening the tap  $l$ . On its way thither it was filtered through the cotton-wool plug  $r$ . The gas was allowed to enter until the mercury in the gauge rose to a certain fixed scale-division  $n_1$ . It was easy to adjust this accurately, provided the capillary had been drawn out fine enough; and in any case small inaccuracies in this adjustment are absolutely without effect on the measurements, as is foreseen from the theory, and as will be confirmed later on. The tap  $l$  having been closed, the effusion was started by opening the tap  $m$  and a stop-watch set in motion as soon as the mercury meniscus sank to a certain scale-division  $n_2$  a little below  $n_1$ . A smooth and easy motion of the falling mercury meniscus was secured by having a small quantity of glycerine in the gauge, *i.e.* just sufficient to lubricate the glass wall but not enough to collect over the mercury. The watch was stopped as soon as the meniscus reached a third fixed division,  $n_3$ . Proceeding in this way with each of the gases to be compared, it will be seen that the times of effusion are measured between exactly the same limits of pressure. The pressure in the receiver at the end of the effusion was measured roughly by opening  $i$  and reading the closed U-gauge. In order to make two consecutive measurements, it was only necessary to open  $i$ , pump out the receiver  $p$ , close  $i$ , and readjust the pressure in the reservoir to  $n_1$  by admitting more gas.

The effusion-plug was made by taking a circular disc of platinum-foil (about  $\frac{1}{25}$  mm. thick), backing it with a flat piece of agate, and piercing it in the centre by gently pressing a very fine needle against it. The disks so constructed were then tested by sealing them to the end of a glass tube with Chatterton cement, and observing the rate of effusion into the exhausted vessel of a Töpler-pump, by noting the rate of fall of the mercury in the vertical capillary.

A suitable disc having been obtained, it was melted off, burnt clean, and soldered with gold to the end of a stout platinum tube, which was finally sealed on to the end of the glass tube  $w$  (Fig. 112). The effusion-aperture employed in the first series of measurements was about  $\frac{1}{50}$  mm. in diameter. Preliminary experiments showed that the time of effusion for any given gas varied somewhat from day to day and—to a less

degree — even during the course of a consecutive series of measurements. This source of error was eliminated by comparing each gas directly with oxygen, and usually the time of effusion for oxygen was measured immediately before and immediately after that of the gas in question, and the mean of these two values taken.

It appeared, however, necessary to introduce a correction for viscosity which was applied by means of the formula,

$$t = a \sqrt{P + b \mu},$$

where  $\mu$  is the viscosity of the gas relative to oxygen,  $b$  is a constant, and  $a$  is a factor dependent on the size of hole.

Assuming that the time required for the effusion of oxygen and hydrogen are proportional to the square roots of their densities, as is highly probable,  $a$  and  $b$  can be calculated.

Oxygen (observed)	.	.	.	676.0"
Hydrogen (observed)	.	.	.	171.6"
„ (calculated from densities)	.	.	.	169.7"

$$676.0 = a \sqrt{16} + b \times 1$$

$$171.6 = a \sqrt{1.008} + b \times .4375$$

$$a = 166.5$$

$$b = 10$$

Applying these results to carbon monoxide

Oxygen (observed)	.	.	.	676.6"
Carbon monoxide (observed)	.	.	.	630.0"

$$t = \left( 166.5 \times \frac{676.6}{676.0} + \sqrt{14} \right) + (.875 + 10) = 632.3"$$

Carbon monoxide (calculated from density)	632.9"
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The results obtained in the case of argon are very interesting; they are tabulated below:—

Oxygen (observed)	.	.	.	673.3"
Argon (observed)	.	.	.	723.9"
„ (calculated from densities)	.	.	.	751.2"
„ (calculated from densities and corrected for viscosity)	.	.	.	751.0"
„ (calculated from the Hugoniot-Reynolds formula)	.	.	.	715.0"
„ (calculated from the Parentz formula)	.	.	.	692.0"

These results show that the abnormality in the case of argon can be attributed to the process of the effusion being partially adiabatic. It appears likely that if the process were truly adiabatic, the Hugoniot-Reynolds formula would express the results fairly exactly.

Helium and carbon dioxide were found to behave in a manner which could not be explained on the assumption of the perfect gas laws. Helium appears to effuse too slowly and carbon dioxide too quickly; this is attributed to the internal work performed by the gas at the jet, which, it is shown, would account for these irregularities. It may be added that in the case of helium the value of  $pr$  appears to increase with increase of pressure to an even greater effect than in the case of hydrogen. It is possible, therefore, that though the Joule-Thomson effect (p. 187) is nearly negligible in the case of the latter gas, it may have a strongly negative value for helium.

*Transpiration.*—The flow of gases in capillary tubes was first studied by Thomas Graham in the early forties (*Phil. Trans.*, 1846). The gases, confined over water in glass vessels, were drawn through capillary tubes of various dimensions into the receiver of an air-pump, and the time required to produce a definite rise of pressure was observed in each case. The conclusions arrived at may be briefly expressed as follows :—

(i) If a gas flows into a vacuum space through a tube whose length is *extremely short*, a mere ring, it will obey the law of effusion. With the slightest elongation the effusion numbers are disturbed, the change being very great at first but soon falling off.

(ii) A tube of any diameter is suitable for transpiration experiments, provided a certain length is given to it.

(iii) The relative time of transpiration of a gas appears to be independent of the pressure, but increases with rise of temperature.

(iv) The time of transpiration of mixed gases appears, in some cases, to be the mean of the two components, but in the case of hydrogen it appears to tend in the direction of slower transpiration; the addition of small quantities of hydrogen to other gases appears to prolong the time of transpiration.

The following figures express the time of transpiration of the commoner gases :—

Oxygen . . .	1.00	Hydrogen . . .	0.14
Carbonic acid . .	0.75	Nitrogen . . .	0.875

*Viscosity; internal friction.*—A stream of gas flowing past a solid surface may be supposed to consist of a number of thin layers parallel to the surface. The layer in contact with the surface may be supposed to be at rest, and, indeed, it has been proved experimentally that the friction between a gas and a solid is, except at low pressures, negligible. Each successive layer moves over the one before it with an increased velocity, and if the stream is moving in the direction of  $x$ , the velocity  $c$  is a linear function of  $y$ , the perpendicular distance from the surface, since the friction between unit area of each layer is the same.

If  $F$  is the tangential force between unit areas of any pair of layers,

$$F = \mu \frac{dc}{dy},$$

where  $\mu$  is a constant, the coefficient of viscosity. If we consider the layers as being at unit distance apart, and moving, relatively, with unit velocity:

$$(ii) \quad F = \mu.$$

Supposing that the gas consists of molecules, there will be a constant interchange between the layers, a quickly-moving layer receiving molecules of higher velocity than those which it gives to the slow-moving layer next to it, this interchange resulting in a tendency to equalise the velocities of the layers. The tangential force will depend upon the number, velocity, and range of action of the molecules, or in other words on the number of impacts between them in unit time. Since at constant temperature, only the number of molecules in unit volume, and their range of action, change, and these two factors change in inverse ratio, the viscosity of a gas should, at constant temperature, be independent of the pressure. This conclusion was arrived at by Clerk-Maxwell in 1860 from his mathematical investigation of the viscosity of gases, and was confirmed by his own experiments. The results obtained by Graham twenty years earlier, pointed in the same direction, and the actual values of the viscosities calculated by O. E. Meyer from Graham's data were confirmatory of Maxwell's law. The subject has been dealt with by O. E. Meyer in a work entitled *The Kinetic Theory of Gases*.

The method employed by Maxwell in his experiments was one which, in a simpler form, had first been applied by 'Coulomb to the determination of the viscosity of liquids. Here three circular discs were fixed rigidly to an axis which was suspended at one end by a fibre, so that if they were rotated they would oscillate about the axis and gradually be brought to rest by friction with the surrounding gas: the viscosity could be calculated from the logarithmic decrement of the period of oscillation. In order to increase the frictional effect of the gas Maxwell introduced four fixed discs *a a a a*, above, below, and between the rotating discs, and very

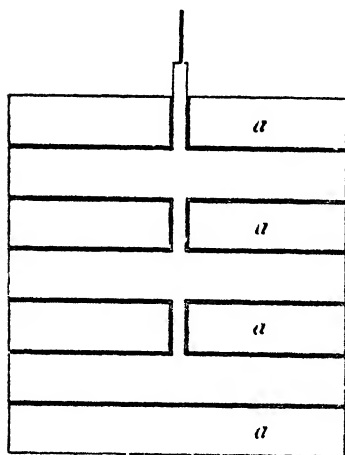


FIG. 123.

nearly touching them. The results showed that Maxwell's law held between pressures corresponding to 10 and 760 mm. of mercury. It appears probable that this method is capable of giving the most accurate results for the absolute values of the viscosities of gases, though, as Kundt and Warburg have shown, it is necessary to apply a correction for the external slipping friction caused by the motion between the moving surface and the gas, when dealing with rarefied gases.

Crookes (*Phil. Trans.*, 1881) employed a rotating vane of mica in the investigation of the viscosities of rarefied gases; the results, which were calculated by the aid of formulae developed by Stokes, showed that the law of Maxwell held good down to very low pressures, but that at extreme rarefaction a sudden change usually occurred.

The relative viscosity of a gas may be determined with a fair degree of accuracy by means of Graham's transpiration method. O. E. Meyer has shown that where  $p_1$  and  $p_2$  represent the pressures at the two ends of a capillary tube of length  $l$  and radius  $v$ , where  $\mu$  is the coefficient of viscosity, and  $v_2$  is the volume of gas which passes through the tube in  $t$  seconds,

$$p_1 r_1 = p_2 v_2 = \frac{\pi t r^2}{16 \mu l} (p_1^2 - p_2^2),$$

$$v_2 = \frac{\pi r^2 (p_1^2 - p_2^2)}{16\mu l p_2},$$

where the driving pressure ( $p_1 - p_2$ ) is constant and not very great. The values of  $r$  and  $l$  would be difficult to determine accurately, but in making comparative measurements their absolute values are not required. In measuring the viscosities of argon and helium Lord Rayleigh employed a tube about 1000 mm. in length and 1 mm. in diameter (*Proc. Roy. Soc.*, **59**, 206), connected at either end with a gas burette and a manometer. During the passage of the gas the pressures were regulated by one of the observers, and it was found possible to adjust them with sufficient accuracy. As a check on the experiments the relative viscosities of hydrogen and air were determined, and the results were found to be satisfactory.

The viscosity coefficient of air is given by O. E. Meyer as 0.000172, the mean of the results of six observers. The value of the coefficient is of the same order for all gases, and even in the case of the monatomic gases no variations are found. The following are the accepted values for the principal gases—

	I.	II.	III.
Oxygen . . .	0.000191	0.000189	
Nitrogen . . .	0.000167	0.000166	
Carbon dioxide .	0.000145	0.000138	0.000152
Hydrogen . . .	0.000084	0.000086	0.000092

I. Calculated by O. E. Meyer from Graham's transpiration numbers. The number 0.899 is given for air referred to oxygen as unity, and the viscosity of air is taken to be 0.000172 at 0° C.

II. Directly determined by Von Obermeyer by the transpiration method at 0° C.

III. Determined by Kundt and Warburg by the method of oscillation at 15° C.; the numbers are, however, somewhat higher than in I and II.

From the transpiration experiments of Lord Rayleigh (*loc. cit.*) the monatomic gases have viscosities

Argon . . . . .	0.000208
Helium . . . . .	0.000165

It may be mentioned here that the viscosity of a gaseous mixture is not necessarily the mean of the viscosities of the



constituents, and, as was shown by Graham, the presence of a small quantity of a gas, such as hydrogen, which has a low viscosity, may increase the apparent viscosity of a gas like carbon dioxide; this fact is in perfect accordance with the kinetic theory. It is necessary, therefore, to take particular precautions with regard to the purity of the gases employed, though, as Lord Rayleigh has shown, the results are not likely to be seriously affected by the presence of *traces* of moisture or of other gases.

The effect of a rise of temperature is to increase the viscosity of a gas. It will suffice to state here that the change is of the same order for all gases, though it might have been supposed that a difference would have been observed in the case of the monatomic gases, since the change in viscosity is dependent not only on the number of the impacts between the molecules, but on the nature of the impacts (Carl Barus, *Am. J. Sc.*, 1888, 408; Holman, *Proc. Am. Acad.*, 1885, 16; Rayleigh, *loc. cit.*; Sutherland (Theory), *Phil. Mag.*, 1893, 386).

*Diffusion of gases.*—This term, though employed by Graham in describing the passage of gases through porous septa, should more properly be applied to the mixing of two gases brought suddenly into contact over a free surface. The subject was studied by Loschmidt of Vienna, and the results published under the title of *Diffusion of Gases without Porous Septa*. A glass tube 1000 mm. long and 25 mm. in diameter was divided in the middle by a thin steel shutter, in which a hole, equal in diameter to the inner section of the tube, was pierced. The two halves of the tube were filled with different gases, and the shutter was moved so as to bring them into contact for a definite period of time. The degree to which the gases had mixed was determined by chemical analysis, and, from the results, coefficients of inter-diffusion were calculated from formulæ developed by Stefan on the basis of the kinetic theory.

The passage of a gas through a porous septum into a vacuum appears to take place partly by effusion and partly by diffusion; the phenomenon is partly molecular and partly hydrodynamic. It is difficult to determine how far each of these phenomena comes into play; but since the rate of flow of the gas is inversely proportional to the square root of its density, it appears to be conditioned by internal friction only to a very slight extent. The method does not, however, lend itself to the determination

of gas densities. The passage of a mixture of gases through a porous septum results in a partial separation of the constituents, the lighter gas passing through in greater quantity. The separation is, however, by no means complete; and even were the phenomenon one of simple diffusion, the concentration of the heavier gas on the first surface of the septum would tend to decrease the efficiency of the process.

The method of fractional diffusion, or atmolysis, was one of the methods employed by Ramsay and Rayleigh to prove that atmospheric nitrogen was a physical mixture (*Phil. Trans.*, 1895, 186, 187). It was also applied to the separation of the constituents of clévite gas (Ramsay and Collie, *Proc. Roy. Soc.*, 60, 206; Ramsay and Travers, *id.* 60, 206).

The gases were introduced through a stopcock E into the diffusion vessel A, which communicated through the porous plug B and the stopcock C with a Töpler-pump. The plug consisted of a piece of tobacco-pipe stem, closed at one end and cemented into the glass tube at the top of the vessel A. Before introducing the gas the apparatus was exhausted through the stopcock D, which was subsequently closed, as was the stopcock C. The rubber tube connecting the mercury reservoir F with the diffusion vessel could be closed by a pinchcock. During the actual experiment the reservoir was adjusted so that the pressure on the gas in the vessel was about equal to the atmospheric pressure.

In the first stage of the experiment the vessel A, after exhaustion, was filled with the gas, which was allowed to *diffuse* through the porous plug into the pump. Five equal fractions were pumped off and collected separately. The first and lightest fraction was then introduced, and after two-thirds of it had passed through the plug, the stopcock E was closed; the gas in the pump was collected to form the first fraction of the second series, and the second fraction was added to the gas in the vessel A. Half this gas was allowed to diffuse into the pump, and the remaining half was mixed with the third fraction and treated in

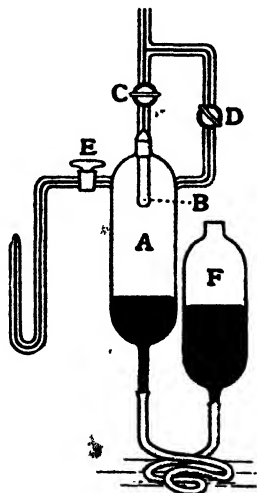


FIG. 124.

the same way. This operation was repeated in the case of each fraction of gas, so as to produce six other fractions. To obtain the sixth fraction it was necessary to open the stopcock D and exhaust the apparatus.

This cycle of operations was repeated about thirty times, with the result that the density of the lightest fraction was reduced to 1.98; the density of the original gas was 2.18. The method is an extremely tedious one to carry out, and is far less effective than fractional distillation as a means of separating gases in a mixture.

## CHAPTER XXI

### REFRACTIVITY

THE first attempt to determine the refractivities of gases is that of Dulong in the year 1826 (*A. de Ch. et de Ph.*, **31**, 154). The gas was introduced into a hollow glass prism, and the pressure was adjusted till a definite deviation was arrived at. The results obtained are closely in accordance with those of modern investigators.

It would be impossible to deal with the various methods which have been applied to the determination of refractivities of gases; the majority of them are based upon the principle of interference, and it is probable, from the widely discordant results which have been published, that the measurements have rarely been made with pure gases.

Although it is only with considerable difficulty that the absolute refractivity of a gas can be determined, it is a comparatively simple matter to determine the ratio of the constants for two gases, or the refractivity of any gas in terms of the refractivity of air, which is taken as unity.

The refractive index  $\mu$ , of any substance, for light of any particular wave-length, is an inverse measure of the velocity with which light of that particular wave-length travels in the substance.

$$\frac{\mu_a}{\mu_b} = \frac{v_b}{v_a}.$$

• The refractivity of a substance is expressed by the symbol  $(\mu - 1)$ , and for matter generally, the law of Dale and Gladstone,

$$\frac{(\mu - 1)}{d} = \text{constant},$$

holds good within narrow limits. In the case of the more perfect gases,

$$\frac{(\mu - 1)}{d} = \frac{(\mu - 1)}{p} = \text{constant.}$$

It is not difficult to attach a physical meaning to the terms  $(\mu - 1)$ . Supposing matter to consist of molecules in the ether, if the time required for the passage of light through a vacuum were unity,  $\mu$  would be the time required for the passage of light through the same space filled with matter.  $(\mu - 1)$  is thus the retardation produced by the presence of the molecules.

Lord Rayleigh (*Proc. Roy. Soc.*, **59**, 203) has devised a very simple apparatus for determining the refractivities of gases, which depends upon the comparison of the velocities of light through identical lengths of two gases by the method of interference. The apparatus was first applied by him to the determination of the refractivities of argon and helium, and subsequently in a slightly modified form by Ramsay and Travers to the examination of the constituents of atmospheric argon.

In the apparatus (Fig. 125, A and B) the gases were contained in two glass tubes *a*, which were connected together and were closed at the ends by optically-worked glass plates. The tubes were cut from a straight length of glass tube about 7 mm. in diameter, and the side tubes were sealed to them; they were then connected together by a broad band of very thin copper sheet, and cement was run into the space between them. The ends *b b'* were then ground perpendicular to the axis, and the worked glass plates, which were only sufficiently large to exactly cover the ends of the tubes, were attached by means of rubber cement. The tubes were then tested for leakage from the outside, and from one tube to the other. The tubes were placed between the two plano-convex lenses *c* and *d*, in such a manner that the middle points of the upper edges of the end-plates lay in the optical axis. The lenses were achromatic, and of about one foot focus; they were mounted on brass tubes, which were attached by cement to slides, which could be moved along the wooden beam on which the apparatus was mounted. The slit *e* was made by drawing a line with a razor across a piece of tinfoil cemented closely on to the second surface of an ordinary piece of glass plate. The slit was

illuminated by means of a paraffin lamp  $f$ , placed at a distance of about 10 cm. from it. A piece of card  $g$ , pierced with two vertical slits, was placed in front of the second lens. These slits were about 4 mm. wide, and their centres coincided with the axes of the tubes. A vertical cylindrical lens was placed at  $m$  to serve as an eyepiece for the observation of the bands formed in the focus of the lens  $d$ . The lens was made from a strip of plate glass which was turned in the lathe with a file and turpentine to about 3 mm. diameter, and was then polished; glass rod would not serve for this purpose. The tubes  $a$  were connected by capillary leads directly to the manometers  $h$   $h'$ , which were provided with adjustable mercury reservoirs  $l$   $l'$ , so that the pressure could be altered at will. The tubes and manometers could be filled with gas through the two-way stop-cock  $A$ , by means of the apparatus described on p. 300, or connected with the pump. The manometers were placed in front of a ruled glass scale, and the readings were taken by means of a telescope.

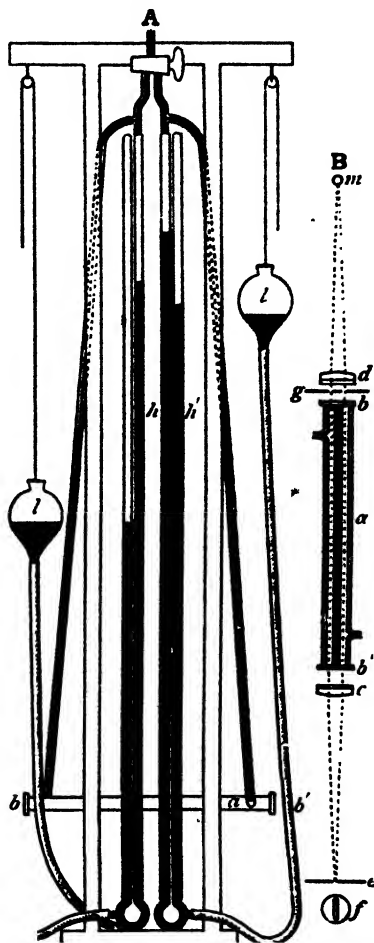


FIG. 125.

The principle of the apparatus is as follows. The diverging beam of light from the slit  $e$  is rendered parallel by the lens  $c$ . From this point we may consider two parallel beams passing partly down the tubes and partly above them, and being brought to a focus by the lens  $d$ . At points in the focal plane of  $b$ , at which the lengths of the paths of the two beams differ by one-half wave-length, interference takes place and bands are formed.

If the sodium flame is employed as a source of light, the bands will be black with bright spaces of yellow light between them; with ordinary white light the dark bands will have coloured fringes. There is no advantage, however, in employing monochromatic light; the dispersion of gaseous matter is so small that the error introduced by the use of white light is too small to be considered in ordinary experimental work, and the coloured bands are quite easily observed. The sharpness of the bands largely depends on the narrowness of the slit.

When viewed with the cylindrical lens two superimposed sets of bands appear. The upper set, which is produced by the beams of light passing over the top of the tubes, acts as a set of fiducial points; the lower set is produced by the beams of light which pass through the tubes. On account of slight irregularities which may exist in the plates or lenses, the two sets of bands will not coincide; this error does not, however, affect the ultimate result.

The tubes and manometers are first thoroughly exhausted; one is filled with the gas whose refractivity is to be determined, and the other with air or with some other standard. If the two gases have the same refractivity, and are at the same pressure, the beams of light will pass with the same velocity through each of them: consequently, the points at which the interference bands are formed will be the same as when they were both filled with air at the same pressure, or were completely exhausted. If their refractivities differ, the velocity of light in the gas of lower refractivity being greater than the velocity of light in the other gas, the bands will be displaced in the direction of lower refractivity. The pressure in the tube containing the gas of higher refractivity is now reduced by lowering the manometer reservoir until the bands in the upper and lower rows exactly coincide. The pressure in each manometer is now read by means of a telescope; and, in order to ensure accuracy, one of the reservoirs is readjusted four or five times, the other remaining fixed.

If it were not for the small irregularities already mentioned it would be possible to calculate the refractivities of the two gases from the ratio of the pressures at which light travelled with equal velocity in each of them. In order to eliminate these errors it is necessary to make the comparison at a second pressure as different

from the first as possible. The reservoir of the manometer containing the gas of low refractivity is now lowered as far as possible, the other reservoir being lowered simultaneously, and a second set of adjustments are made. In lowering the reservoirs there is some danger of mistaking the bands which should correspond. This difficulty may be got over by lowering both reservoirs, so that no great displacement ever occurs. The difficulty becomes much greater with heavy gases, when a great number of bands pass across the field for a small change of pressure.

From the differences between the results of the two sets of readings the refractivities may now be directly calculated.

If  $p_a$  and  $p_b$  are the pressures after the first adjustment, and  $p'_a$  and  $p'_b$  the pressures after the second adjustment,

$$\frac{p'_a - p_a}{p'_b - p_b} = \frac{\mu_b}{\mu_a}.$$

*The standard.*—If the relative value of the refractivity of the gas lies between 0·5 and 1·4, one manometer is filled with air. In measuring the refractivities of gases, such as helium or neon, some difficulty was experienced, as it was necessary to lower the pressure on the air considerably in order to bring the bands into position on the field, and unless the manometer tubes were very long it was found to be impossible to obtain a second set of readings differing greatly from the first. It was found to be more convenient to measure the refractivities of these gases against hydrogen, and to determine the constant for that gas against air by a subsequent series of measurements.

*Refractivity of argon in terms of air as unity.*—The pressure differences are expressed in millimetres of mercury:—

	Argon.	Air.
First difference	7·7	13·6, 13·3, 13·6, 13·0, 13·3; mean, 13·36
	Argon.	Air.
Second difference.	368·2	361·0, 361·5, 361·2, 361·0, 361·3; mean, 361·2
	Refractivity = $\frac{361·0 - 13·36}{368·2 - 7·7} = 0·9679.$	
	Argon.	Air.
First difference	8·0	12·9, 12·7, 12·6, 12·6, 12·7; mean, 12·7
	Air.	Argon.
Second difference.	355·1	361·1, 361·8, 362·0, 361·0, 361·5; mean, 361·5
	Refractivity = $\frac{355·1 - 12·9}{361·5 - 8·0} = 0·9680.$	



The following values were obtained for the refractivities of the principal gases :—

	$\mu - 1$ .
Air . . . . .	1·000 <sup>1</sup>
Hydrogen . . . . .	0·473 <sup>1</sup>
Oxygen . . . . .	0·924 <sup>1</sup>
Nitrogen . . . . .	1·016 <sup>1</sup>
Neon . . . . .	0·2345 <sup>2</sup>
Argon . . . . .	0·9655 <sup>2</sup>
Helium . . . . .	0·1238 <sup>2</sup>
Krypton . . . . .	1·449 <sup>2</sup>
Xenon . . . . .	2·361 <sup>2</sup>

<sup>1</sup> Ramsay and Travers, *Proc. Roy. Soc.*, **62**, 228.

<sup>2</sup> *Id.*, **64**, 190.

<sup>3</sup> *Id.*, **67**, 331.

## CHAPTER XXII

### SPECTRUM ANALYSIS

Historical note—Gases for examination—Vacuum-tubes and electrodes—Method of filling vacuum-tubes—Qualitative observations—The spectrometer—Standard lines—The induction coil—Electric discharges in vacuum-tubes—The nature of luminous spectra—Spectra of hydrogen, helium, neon, argon, krypton, xenon, mercury, nitrogen, and the oxides of carbon.

It was first noticed by Plücker (*Pogg. Ann.*, cvii. 497) in 1859 that the nature of the light emitted by the so-called Geissler tubes depended upon the gas with which they were filled. This observation led to the application of the methods so successfully employed by Bunsen and Kirschhoff in the examination of solid substances, to the investigation of the spectra of gases.

*Gases for examination.*—The preparation of gases in a state of purity has already been dealt with at length, and it only remains to add a few remarks with regard to precautions to be taken if a gas is intended for spectroscopic examination. Since in a mixture of gases the nature of the spectrum depends only within certain limits on the proportion of the constituents present, and since certain gases, such as the various compounds of carbon, have a considerable influence even when present in minute quantity, it is essential that the processes of preparation and purification shall be so selected that these substances are entirely absent. Further, if the examination is conducted with a view to determining the nature of a chemically inactive residue (helium, etc.) the gas should be previously sparked with oxygen (p. 104), and the oxygen subsequently removed by means of phosphorus.

*Vacuum-tubes.*—In order to observe the spectrum the gas is introduced into an exhausted tube at a pressure of 2 to 3 mm. Under the influence of the electric discharge, produced by connecting the secondary terminals of an induction coil with the

electrodes which are fused into the tube, the gas emits a characteristic glow which is analysed by means of the spectroscope.

The tubes, commonly called Plücker tubes, which are used to contain the gas, are shown in Fig. 126. In *a* the capillary portion of the tube, which should have an internal diameter of about 1 mm., is sealed to two wider portions containing the electrodes which lie in the axis of the tube. When in use the capillary portion of the tube is placed opposite and parallel to the slit of the spectroscope. The tubes *b* and *c* are so constructed that when placed opposite to the slit the axis of the capillary lies in the line of collimation. By this means the intensity of illumination is much increased. In *c* the tube is closed by a quartz plate which is cemented to the end of the tube which is ground flat.

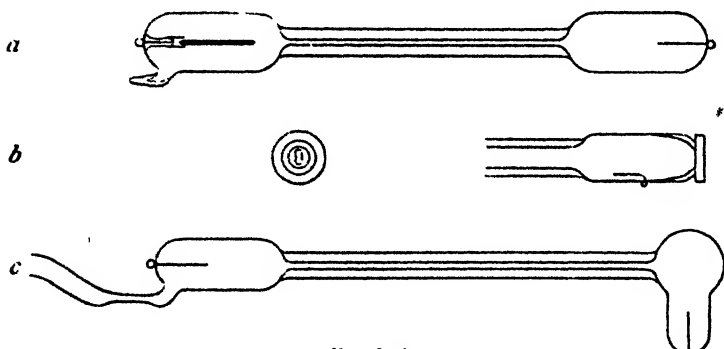


FIG. 126.

The object of the quartz plate is to admit of the passage of ultra-violet rays, to which glass is opaque, and which can only be detected by photographic methods. In these "end on" tubes the capillary is often flattened.

The electrodes which pass inside the tubes may be either of aluminium or of platinum, preferably of the former, sealed into the tube by means of a little lead, glass, or enamel. If platinum electrodes are used they can be easily introduced in the following manner. The different stages of the operation are shown in Fig. 127. A piece of platinum wire about 2.5 cm. long is bent into a loop (*a*), and while held in the forceps in the blowpipe flame, a stick of enamel is melted, and drawn round it so as to leave a bead of the material on the wire close to the loop; the wire is also thinly coated with the enamel for about half its length

(b). The wide portion of the vacuum-tube, previously sealed to the capillary, is then drawn to a point, and the point is heated in the flame and blown out so as to leave an opening rather smaller than the knob of enamel on the platinum wire (c). The wire is then placed in position, and the end of the tube strongly heated with a small flame till the glass and enamel are thoroughly melted; the tube is then blown out and melted down a second time. This operation should be repeated several times, when the enamel should form an even ring about 5 mm. wide round the wire (d). The side-tube should then be sealed in position, and the second electrode introduced.

Platinum electrodes are little used, especially if the tubes are to be much used, as they become very hot, and the platinum

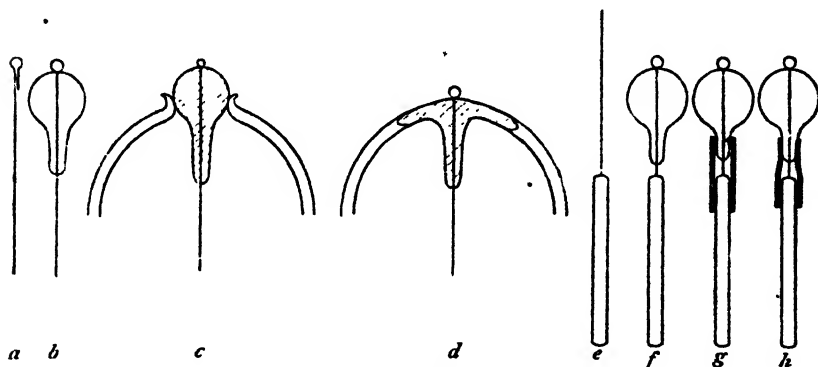


FIG. 127.

volatilises under the influence of the discharge. This would of itself be unimportant, but for the fact that the metal, which is deposited on the walls of the tube, is in the amorphous condition at the moment of deposition and able to absorb certain gases, particularly helium. Aluminium, on the other hand, although it too is volatile to a certain extent in the inactive gases, does not appear to absorb them so quickly, though it completely absorbs traces of nitrogen, carbon monoxide, etc.

An aluminium electrode is made by heating the end of a piece of aluminium wire in a fine blowpipe flame, and when it is just melted bringing it into contact with a piece of platinum wire *e*; a trace of pure gold on the platinum facilitates the union of the two metals. The platinum wire is then cut to the right length, bent and coated with enamel for the greater part of its

length, leaving a knob of enamel near the loop (*f*). In order to completely protect the platinum a short piece of thin glass tube is slipped over the aluminium wire, so that this covers the junction and reaches nearly to the knob of enamel (*g*). By heating in the blowpipe flame the enamel and glass are sealed together (*h*), and the electrode is sealed into position in the tube. Recently I have employed electrodes in which the aluminium wire is drilled through its whole length, and threaded with stout platinum wire. Such electrodes, even should they become very hot, cannot fall against the side of the tube and crack the glass.

It is sometimes convenient to use tubes with one platinum and one aluminium electrode, for on account of the intermittent

nature of the discharge from an ordinary induction coil only one electrode, the cathode, becomes strongly heated. For reasons which will be given later, the side-tube is placed at the end nearest to the aluminium electrode.

*Method of filling vacuum-tubes.*

—The apparatus employed for this purpose is shown in Fig. 128. The tube A is sealed to the mercury-pump, with which the apparatus communicates through the stopcock B. The vacuum-tube is sealed to the tube C, which contains phosphorus pentoxide confined between plugs of glass wool. This tube is removed when the pentoxide is exhausted, and replaced by another freshly-filled tube. The gas is introduced through the syphon D, and if the apparatus is constructed as in the figure there will be little danger of pellets of mercury being carried into the

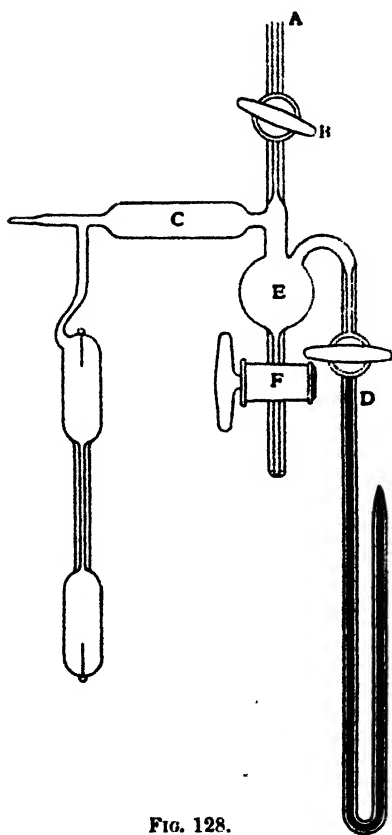


FIG. 128.

pentoxide tube or into the tube leading to the pump.

The apparatus is first thoroughly exhausted, and mercury is

drawn into the syphon to the level of the top of the stopcock by raising the trough (p. 26, Fig. 28) till the point is below the surface of the mercury, and opening the cock. During the latter stages of the exhaustion the vacuum-tube is heated with a Bunsen burner, and a strong electric discharge is passed between the electrodes, which are attached to the terminals of an induction coil. The direction of the discharge, which is *intermittent* (p. 309) in character, should be reversed every two or three minutes to ensure that both electrodes are thoroughly heated. The spectrum of the last traces of gas in the tube will probably be that of hydrogen, produced mainly by the decomposition of the water driven off from the glass by the action of heat. The heating and exhaustion are continued till the glass begins to glow with a brilliant yellow-green phosphorescence, or till the discharge will no longer pass between the electrodes inside the tube.

With aluminium electrodes the discharge must be passed for a longer time than if platinum electrodes are used, as the metal appears to give off hydrogen as it becomes hot. With aluminium electrodes there is, however, the advantage that traces of nitrogen and carbon compounds are rapidly absorbed by the metal. For this reason it is not unusual to employ a single aluminium electrode, the other being of platinum. The aluminium electrode is always placed at the top and connected with the cathode terminal of the coil when the tube is in use, for if it should then become hot and melt it will not fall against the side of the tube and crack the glass.

It is sometimes extremely difficult to remove carbon dioxide, etc., from the tube by simple exhaustion; in this case a little air should be admitted and the tube re-exhausted.

When the exhaustion is completed the stopcock B is closed, and the tube containing the gas to be examined is brought over the upturned end of the syphon in the mercury-trough. The stopcock is then turned so that the gas enters the syphon, driving the mercury into E, and finally passes into the apparatus. The quantity of gas which enters the apparatus can easily be regulated, and in adjusting the pressure so as to produce the best effect the direct vision spectroscope is brought into use. The vacuum-tube is sealed from the apparatus by heating the capillary tube with a fine blowpipe flame. Mercury is then drawn into the syphon, and

the remaining gas is removed from the apparatus through the pump and collected.

If the gas contains traces of nitrogen or oxides of carbon, the impurity is rapidly absorbed by the aluminium electrode when the tube has been in use for a short time.

If a number of specimens of gas are to be examined qualitatively with the direct-vision spectroscope they may be introduced one after the other into the same tube, which is merely exhausted between each operation. Care must be taken that the syphon is filled with mercury before a new sample of gas is introduced.

*Mercury vapour in vacuum-tubes.*—When an apparatus of this kind has been in use for some time, it is frequently found that the spectrum of the gas introduced into it contains the green and yellow mercury lines. This is very marked among the gases of the helium group, particularly the heavier members, but though it depends to some extent on the gas, it is chiefly caused by small particles of mercury being carried through the whole apparatus and volatilised by the heat generated in the tube.

The introduction of mercury vapour into the tube may be partially prevented by introducing at the end of the tube E a tube filled with gold-leaf. In order to retain all traces of mercury vapour the following method has been used with success. A tube of about 20 cm. long and 1 cm. in diameter is packed with layers 4 cm. long of the following substances—

- (i) Silver foil.
- (ii) Sulphur.
- (iii) Iodine.
- (iv) Sulphur.
- (v) Silver foil.

The tube is introduced between the pentoxide tube and the vacuum-tube. It is somewhat difficult to exhaust through it on account of the vapour pressure of the iodine. When it is not in use air should be admitted to the apparatus in order to diminish the rate of diffusion of the iodine and consequent wasting of the tube.

*Qualitative observations.*—For qualitative observations it is convenient to employ the prismatic combination of a direct-vision spectroscope, without slit or lenses. If the capillary of the vacuum-tube is narrow the lines will appear very sharp and

brilliant. For observations on the nature of the glow round the electrodes in the tube a spectroscope with slit and lens must be used.

*The spectrometer.*—Although with a little practice it is possible to recognise the spectra of the principal gases, and to detect the presence of two or more gases in mixtures without reference to a scale, it is often necessary to obtain more conclusive proof of the identity of a line or of its position in the spectrum. For this purpose it is necessary to employ either a spectrometer, in which the deviation of the line may be directly

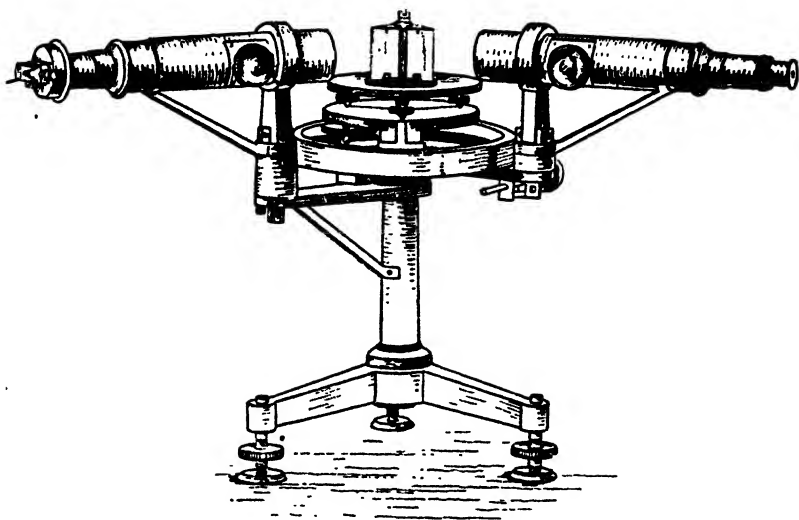


FIG. 129.

observed, or a spectro-photometer. The latter instrument is for many reasons always employed when a number of accurate measurements are required; space does not, however, permit of a description of the methods of spectro-photography. It is possible to measure the wave-length of a line to the nearest Angström unit, one ten-millionth of a millimetre, by means of a spectrometer with a 20 cm. circle and a prism of high dispersive power. Since, however, the accuracy of the results will depend in a great measure upon the structure and manipulation of the instruments, it may be well to mention the more important points to be attended to.



The instrument should be built upon a solid cast-iron stand, which can be levelled by means of screws resting on counter-sunk plates. The screws should be at least 1 cm. in diameter, and should fit accurately into their sockets. The vertical pillar supports the divided circle, 20 cm. in diameter, and 1 cm. in thickness. The circle may be divided on its horizontal or vertical surface, preferably on the latter. In either case the accuracy is the same, but the vertical divisions have the advantage that they can be read by means of a horizontal microscope, and that the vernier graduations lie in the same plane with them; graduations on a bevelled surface are not to be recommended.

The prism-table should be raised as little as possible above the circle. It should be capable of being rotated about the vertical centre of the instrument by a pinion working into a rack on the edge of the table. An arm projecting from the table carries a vernier, by means of which the position of the table can be determined.

The tube, which carries the slit and collimating lens, is usually attached to a support rigidly fixed about the zero of the circle. The support must be so constructed that the collimator is capable of slight horizontal and vertical adjustment, and is at the same time rigid and free from vibration. Both the telescope and collimator should be carried on their supports in draw-tubes, into which they fit well but easily, and are secured by clamping screws. It should be possible to remove the telescope, and replace it without altering the reading of the instrument.

The telescope is supported on an arm capable of free rotation about the vertical centre, so that its axis may be made to coincide with the axis of the collimator. The arm carries a vernier by means of which the position of the telescope with regard to the divided circle is determined. Spectrometer circles are often provided with two verniers, but if the instrument is well made the eccentricity, which the second vernier is intended to correct, is negligible. The telescope can be moved into position by hand. The final adjustment is made by means of a micrometer screw attached both to the rotating arm and to a block, which can be clamped at will on to the edge of the circle in any position. The screw should be of low pitch, and it should be possible to take up wear.

Considerable difficulty has been experienced in constructing

a telescope support so that it is quite free from vertical motion. In the best spectrometers the telescope arm is pivoted on the stand-pillar, which it grips for a considerable section of its height.

The collimator and telescope each carry an achromatic plano-convex lens of 25 to 30 cm. focus; the shorter length is the more convenient for ordinary use. The slit is carried at the end of a slide-tube which has a rack and pinion adjustment. The slit itself should be made of some non-corroding metal; one jaw should be fixed, and the other capable of adjustment by means of a micrometer screw; the two components are kept apart by a spring. In order to reduce the vertical width of the slit a shutter with a V-shaped slot in it is made to slide over its first surface. A small right-angle glass prism, which can be adjusted so as to cover half the slit, serves to throw light from a source at the side down the tube.

The eyepiece, which is used either for comparative observations or for measurements of angular deviation, must contain a spider line or pointer in its focus, which must be brought into coincidence with the line under observation. If the line is a faint one it is almost impossible to determine when the cross-wire or pointer is exactly over it, but the difficulty can be overcome by employing an eyepiece in which the pointer is illuminated from a separate source. For convenience in adjusting the instrument the needle may be made to move across the field by means of a screw.

*Method of using the spectroscope.*—Before the telescope is placed in position it should be focused for parallel light by observing some distant luminous object, preferably the moon. Since it is necessary to alter the focus of the telescope in observing lines in different parts of the spectrum it is convenient to have the tube which carries the eyepiece graduated in millimetres, so that a portion can at any time be recovered. The telescope and collimator are placed opposite to one another; the slit is illuminated by means of a sodium flame, and adjusted so as to obtain the sharpest image. The tubes are then adjusted in the horizontal and vertical position till their two axes exactly coincide. In its operation the slit should be reduced by means of the horizontal slide to a luminous point, and its image should occupy the centre of the field of the telescope. The position of the telescope should be read off on the circle and noted

Each prism should be permanently fixed to a stand resting on three levelling-screws. The points of the screws should rest in the radial slots which are cut in the surface of the prism-table, so that the prism can be removed and replaced in its original position. If it is necessary to place the prism somewhat to one side of the prism-table one of the screws may rest in one of the slots, one on the surface of the table, and one in a small hole drilled specially to receive it.

The prism is then adjusted to the position of minimum deviation by moving the telescope and prism-table; the positions of both are carefully noted. For visual measurements of wavelengths it is sufficient to make the adjustment for the middle of the spectrum, the hydrogen F line. If the prism is not placed in the position of minimum deviation, except for perfectly parallel light, the lines will be doubled, or at least blurred.

After placing the prism in the position of minimum deviation a further adjustment of the collimator may be made by Schuster's method (*Phil. Mag.*, 1879, 7, 95). The prism is placed in the position of minimum deviation, and the telescope is so placed that the cross-wire lies slightly on the more refrangible side of some clearly defined line, such as the D line. There will thus be two positions of the prism in which the line will coincide with the cross-wire. The prism table is first turned in the opposite direction to that in which the telescope was previously moved, till the line coincides with the cross-wire; the telescope is then adjusted to the focus. The prism is thus moved to the second position in which the line and cross-wire coincide, and the focus is again obtained by adjusting the position of the slit. These two operations are repeated till the line appears in focus for both positions of the prism. This method has the advantage of adjusting the instrument for parallel light for a much wider range of the spectrum than is possible by the ordinary method.

*Comparison of Spectra.*—If the spectra of two gases are to be compared in order to detect the presence of coincident lines, one vacuum-tube is placed directly in front of the slit and the other at the side, so that the light is thrown into the tube by means of the small right-angle prism, which is adjusted so as to cover half the slit. The spectra are seen in the telescope exactly superimposed, and by making the cross-wire coincide with them it is easy to determine the presence or absence of coincident lines.

It is also possible to compare the lines in the spectra of two gases by placing the tubes in turn before the slit and adjusting the cross-wire or pointer to the line in question.

In order to determine the deviation of any line the telescope is adjusted so that the line coincides exactly with the spider line or with the bright edge of the pointer. In making the adjustment the tangent screw should be released from the circle, and the telescope moved by hand till the coincidence is almost exact; *the hand should be placed on the support close to the circle and not on the tube.* The clamp on the fine adjustment is then made fast, and the pointer brought exactly into position. The position of the telescope is then determined by means of the circle and vernier.

*Micrometer screw eyepieces* are sometimes used in the determination of small differences of wave-length, but since it is much easier to make accurate measurements by photographic methods these instruments do not possess any great advantages.

From the deviation obtained from the vernier reading it is possible to determine the wave-length or oscillation frequency of the line under observation by reference to a curve obtained by plotting on ruled paper the values for known lines against the arc readings of the spectroscope. A curve representing oscillation frequencies is by far the most convenient, as it approaches much more nearly to a straight line: the wave-lengths can be determined from the wave frequencies by reference to a table of reciprocals. The lines on the spectra of the gases argon, helium, hydrogen, and of the vapour of mercury cover a considerable range, and the gaps may be filled in by the lines in the arc spectra of certain metals. The following list of lines will serve for the calibration of an instrument within the limits of the visible spectrum, that is to say for radiation of wave-length between 7600 and 4000 tenth-metres.

*Standard wave-lengths.*—To eliminate errors which might be introduced through the use of different absolute standards of length it is usual at the present time to refer all wave-lengths to Rowland's standard. Rowland's scale of wave-lengths differs from that of Angström, and it is necessary to apply to the latter a correction varying from 1.7 units for the B line downwards. Rowland's wave-lengths are expressed for air at 20°; they may be corrected to vacuo by reference to a table.

## STANDARD LINES EMPLOYED IN CALIBRATION

		1	Measured by
F	Potassium . . . . .	{ 7699.3 7665.6	
	Solar A . . . . .	7607.8	Rowland.
T	Argon (red pair) . . . . .	{ 7066.6 6964.8	Eder and Valenta.
	Solar B . . . . .	6870.2	Rowland.
F	Lithium . . . . .	6708.2	
T	Helium . . . . .	6677	Runge and Paschen.
T	Hydrogen C . . . . .	6563.1	
S	Cadmium . . . . .	6438.8	
F	Lithium . . . . .	6103.8	
F	Sodium D <sub>1</sub> . . . . .	5896.16	Mean of determinations by Angstrom, Thalen, Kurlbaum, Muller and Kempf, Pierce, and Bell; taken by Rowland as his standard.
F	Sodium D . . . . .	5890.19	
T	Helium . . . . .	5875.9	Runge and Paschen.
T	Mercury . . . . .	{ 5790.5 5769.5	Eder and Valenta.
S	Copper . . . . .	{ 5782.90 5700.39	Rowland.
T	Argon . . . . .	5651.0	Eder and Valenta.
T	" . . . . .	5607.4	"
T	" . . . . .	5559.0	"
T	" . . . . .	5496.2	"
T	Mercury . . . . .	5461.0	"
T	Argon . . . . .	5452.0	"
S	Cadmium . . . . .	5379.3	"
	" . . . . .	5338.6	"
S	Copper . . . . .	5292.75	Rowland.
	" . . . . .	{ 5220.28 5218.45	" (pair)
	" . . . . .	5153.40	"
	" . . . . .	5105.75	"
S	Cadmium . . . . .	5084	Eder and Valenta.
T	Helium . . . . .	5015.73	Runge and Paschen.
T	Hydrogen F . . . . .	4861.5	Rowland.
T	Helium . . . . .	4922.10	Runge and Paschen.
S	Cadmium . . . . .	{ 4799 4677	Eder and Valenta.
T	Helium . . . . .	4471.65	Runge and Paschen.
	Cadmium . . . . .	4416	Eder and Valenta.
T	Helium . . . . .	3888.78	Runge and Paschen.
	Cadmium . . . . .	3611	Eder and Valenta.

Abbreviations: T, vacuum-tube; S, spark between electrodes of the metal; F, flame spectrum.

*The induction coil.*—For the production of spectra, for sparking gases with oxygen, etc., an induction coil, capable of giving a six-

inch spark, should be employed. The coil should be a good one, by Apps, Newton, or some well-known maker; cheap coils quickly wear out, and owing to the breaking down of the insulation of the secondary circuit soon cease to be efficient. The coil should be kept dry and free from dust, and care should be taken that the platinum contact-pieces are in good condition; when they become rough they should be carefully filed.

An Apps coil giving a six-inch spark in air works well with four accumulator cells in series. The secondary discharge is of an intermittent nature, the *effect* produced at the cathode, the region of maximum disturbance, being different from that produced at the anode. The intensity of the secondary discharge may be regulated by adjusting the tension on the spring of the armature by means of a screw. The adjustment should not be made by means of the contact screw, which should only be moved in order to take up wear on the platinum contact-pieces.

The alternating current may be used with effect in sparking gases with oxygen, and in producing brilliant spectra with vacuum-tubes. The terminals of the primary coil are connected through a resistance, so as to reduce the current to about five ampères, with the leads from the main, and the armature is screwed up so as to bring the contact-pieces together. On turning on the current the coil emits the well-known "transformer hum," and an alternating current of high intensity is produced in the secondary coil. If the spark-points are brought close together an electric flame is produced between them; this flame is very efficient in effecting the combination of oxygen and nitrogen. Since the secondary discharge in a vacuum-tube is in this case truly alternating, no difference is observed at the two poles, and both electrodes become equally heated.

A remarkable change in the nature of the discharge, and consequently in the nature of the spectra, is produced by the introduction of a Leyden-jar and spark-gap into the secondary circuit. The effect is to produce an oscillatory discharge of high intensity. The outer coating of the jar is connected with one terminal, the inner coating with the other, and the spark-gap is placed in circuit with the tube. The width of the spark-gap may vary between one and seven millimetres, and should be adjusted so as to produce the maximum effect.

*Luminous spectra* may be divided into two classes: bright

line spectra, in which the luminous regions are sharply defined at the edges, and correspond to light of definite vibration frequency; and band spectra in which the regions of maximum and minimum intensity shade off into one another. Band spectra usually consist of a number of bright lines close together.

There appears to be no direct connection, at least so far as is at present known, between the nature of a gas and its spectrum, for it cannot even be assumed that a simple bright line spectrum necessarily indicates 'a simple molecular structure. Certain relationships have, however, been found to exist between the vibration frequencies of the lines in the spectra of individual gases, as in the case of helium by Runge and Paschen (p. 311), and also between the spectra of substances closely allied.

The nature of the spectrum of any gas depends upon the conditions under which it is produced, and may be considerably influenced by the nature of the electric discharge in the tube, by the pressure under which it is confined, and by the presence of other gases. The nature of the discharge between the secondary electrodes of an induction coil, and the effect of introducing a Leyden-jar and spark-gap into the secondary circuit, has already been referred to, and by means of this arrangement very striking changes can be produced in the spectra of certain gases such as argon and xenon. The spectrum of helium undergoes a change when the pressure is altered: under a pressure of 5 mm. the glow emitted by the gas is yellow and the line of maximum intensity is  $D_3$ , 5876; when the pressure is reduced the glow becomes green and the line 5016 predominates. The effect of pressure on the spectrum of a mixture is very marked; helium, for instance, is entirely obscured by nitrogen at high pressures, while at low pressures only the helium is visible.

The prism spectra of certain gases have been specially photographed for this book, and are reproduced on the accompanying plates. I am indebted for these photographs to Mr. E. C. C. Baly and Mr. Mees.

The principal lines in the spectra of the elementary gases are given in the following tables. Fuller lists will be found in any work on spectroscopy, or in Watts's *Index of Spectra*.

*Hydrogen*.—The spectrum of hydrogen contains the following lines:—

C	.	.	$\lambda = 6562.1$
F	.	.	4861.5
			4340.7
			4102.8

The so-called secondary spectrum of hydrogen consists of a vast number of fine lines filling the whole of the spectrum. It is certain that absolutely pure hydrogen is very difficult to obtain, but whether the secondary spectrum is due to hydrogen at all is still a moot point.

*Helium.*—Under the influence of the intermittent discharge the spectrum of the gas contains the following lines:—

7056 (Not coincident with argon, Kayser, <i>Chem. News</i> , 1895)
6677
5875.9 ( $D_3$ , weak component 5876.2)
5048 (Easily masked by impurities)
5015.6
4922
4713
4472

At 7-8 millimetres pressure the colour of the glow in the tube is brilliantly yellow, and the line  $D_3$  reaches its maximum intensity. On reducing the pressure, the intensity of 5015.6, the green line, increases, and at 1.2 mm. the tube emits a brilliant green light; this only happens when the gas is pure. This phenomenon led Runge and Paschen to believe that they had effected a separation of helium into two substances which were characterised by the lines 5875.9 and 5015.6 respectively.

The line 7055 disappears when the jar and spark-gap are used; the spectrum is not, however, otherwise affected, only becoming rather less brilliant.

In the presence of other gases, particularly those like nitrogen which give a compound spectrum, the helium lines are most easily distinguished when the pressure is very low; the green line (5016) is usually the most brilliant (Ramsay and Collie, *Proc. Roy. Soc.*, **59**, 258) (see Fig. 130).

*Neon.*—The lines in the spectrum of this gas lie for the most part within the red area; these are strong and brilliant, as is also the yellow line  $D_2$  (5852.6). There are also strong green lines. The glow in the vacuum-tube is a red-orange, which becomes rosy if much helium is present in the gas; the presence of this gas is



most easily detected by means of the green line 5016. The spectrum of neon is weakened, but not changed when a Leyden-jar and spark-gap are introduced into the secondary circuit. The wave-lengths of the lines have been measured by Mr. Baly by means of a Rowlands grating.

*Argon.*—The spectrum of argon is very complex in character, and undergoes a striking change when the nature of the discharge is altered. With the intermittent discharge the glow in the tube is red, and few blue lines appear in the spectrum; with an oscillatory discharge the glow is bright blue, the red lines in the spectrum disappear, or become faint, and many new green and blue lines appear; when the gas in the tube is at low pressure it usually gives a mixture of the two spectra. With a Tesla discharge the glow becomes nearly white and a spectrum akin to the blue spectrum appears; while on the other hand by passing an alternating current of low voltage through the primary circuit of the induction coil, the red spectrum is produced with the line 6964·8 strongly intensified. It appears then that the red and the blue spectra are themselves capable of further modification (Kayser, *Berlin Akad.*, 1896: Eder and Valenta, *Wiener Akad.*, 1896).

Red Spectrum.	Blue Spectrum.
7056·6— Very bright	
6964·8— pair.	
6752·7— Faint pair	
6676·5—	
6415·2 Strong line	
6212·5— Faint pair	
6172·9—	6172·3 Weak line
	6114·1 „
6033·7 Strong line	6033·7 Strong line
5912·5— Fairly strong	
5889·0— pair	
5739·9 Fairly strong	5739·9 Fairly strong
5651·0—	5651·0
5607·4	5607·4
(5572·9) Group containing * five strong lines	5559·0 Lines much weaker than in red spectrum
5496·2	5496·2
5451·9	5451·9
(5421·7)—	
5253·8—	5253·1
5221·6 Group of	
5187·5 four lines	
5162·6—	

The lines in the blue part of the spectrum can only be accurately identified by direct comparison, or by photographic methods (see Fig. 130).

In the presence of small quantities of nitrogen the argon spectrum is invisible. In such cases the spectrum is more easily seen when the pressure is low and the jar discharge is employed.

*Krypton.*—Like helium and neon the spectrum of the gas is independent of the nature of the discharge. The lines in the red area are few, but bright and distinct. The yellow line, 5871, and the green line, 5570·5, are by far the most brilliant, and like the mercury line, 5461, they are distinctly visible when the gas is only present in minute quantity in a mixture. These lines are probably present in the spectrum of the aurora-borealis, though this requires confirmation, and also in the spectrum produced by the passage of an electric spark through liquid air. The glow in the tube is yellow-green (see Fig. 130).

*Xenon.*—The spectrum of this gas, like that of argon, undergoes a change when a Leyden-jar and spark-gap is introduced into the secondary circuit, but of an inverse order. With the intermittent discharge the glow is blue and the lines in the red and green parts of the spectrum are few and faint. With the jar and spark-gap the glow becomes green and very brilliant, and the spectrum, which is very complex, contains many green lines (see Fig. 130).

*Halides of carbon and silicon.*—The line spectra of these gases are remarkably brilliant. The wave-lengths of the lines will be found in Watts's *Index of Spectra*.

*Mercury.*—The spectrum of mercury, like that of krypton, is visible in the presence of traces of the substance only. Vacuum-tubes when newly filled with the rare gases, particularly those of higher atomic weight, almost invariably give the spectrum of mercury. In a short time, however, the mercury appears to be absorbed by the electrodes, and the lines of its spectrum disappear.

Lines in the spectrum of mercury (Kayser and Runge):—

5790·5	5461·0
5769·5	4358·6

*Banded spectra—Oxygen, Nitrogen, Oxides of carbon*

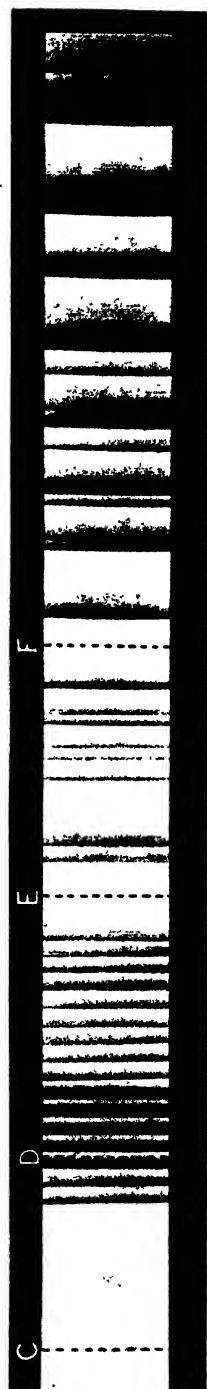
It is impossible to enter on a description of the spectra of the substances mentioned above, or the changes which they undergo under varying conditions. A very brief account of their general characteristics must suffice.

*Oxygen.*—The whole spectrum of the light from the capillary portion of a Plücker tube is faint, and consists only of some lines in the red and a number of indistinct bands extending through the blue portion of the spectrum. The glow in the tube is yellowish, and persists after the discharge has ceased to pass.

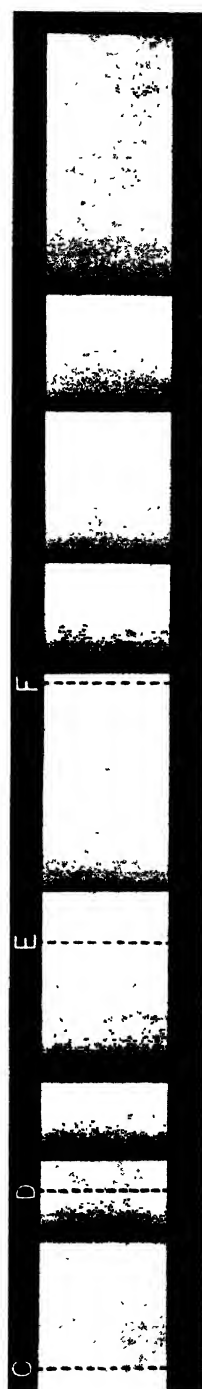
The presence of oxygen considerably weakens the intensity of the spectra of such gases as helium; the visual spectrum of air is, however, identical with that of nitrogen.

*Nitrogen.* --The brilliant banded spectrum of the light from the capillary portion of a Plücker tube is very characteristic but difficult to describe. The accompanying photograph gives a good idea of the position and form of the bands (Fig. 131).

*Oxides of carbon.* -- There appears to be some confusion between the spectra assigned to the two oxides of carbon, and many physicists have assigned to the dioxide,  $\text{CO}_2$ , the spectrum which is probably due to the monoxide,  $\text{CO}$ , and which may sometimes be produced by the decomposition of the former under the influence of the discharge, or in contact with the heated electrodes in the vacuum-tube. The true spectrum of pure  $\text{CO}$  is practically identical with the so-called Swan spectrum of the luminous gas flame. The spectrum of  $\text{CO}_2$  is much less sharp, and contains fewer bands. The matter has recently been made the subject of an investigation by Smithells (*Phil. Mag.*, 1901, **1**, 476).



Nitrogen.



Carbon dioxide.

Fig. 131.



## APPENDIX

### METHODS OF MAINTAINING A CONSTANT TEMPERATURE

THE simplest method consists in surrounding the apparatus with a melting solid, so that the liquid produced is continually removed, or the mixture of solid and liquid is well stirred. As a rule ice only is employed, but other solids, such as naphthalene (M.P. 80·06), and certain salts at their transition points, may be employed (Richards and Churchill, *Proc. Amer. Acad.*, 1899, **34**, 277; Richards, *Zeit. Phys. Chem.*, 1890, **26**, 690; Chappuis, *Les Echelles Protiques*, 1900, 17).

#### TEMPERATURES ON THE NORMAL SCALE p. 149)

Ice	.	.	.	.	0·0°
Mercury	.	.	.	.	- 38·80
$\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$	.	.	.	.	+ 19·85
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	.	.	.	.	32·379
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	.	.	.	.	35·1
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	.	.	.	.	48·0
$\text{NaBr} \cdot 2\text{H}_2\text{O}$	.	.	.	.	50·7
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	.	.	.	.	57·8
$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	.	.	.	.	61·0
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	.	.	.	.	73·4
$\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$	.	.	.	.	77·9

If ice is used in delicate experiments it should be made from distilled water; this is not, however, important except in the case of instruments such as the Bunsen ice-calorimeter, which appears to be affected by the change of melting-point consequent upon change of atmospheric pressure.

By circulating water from the main through a jacket surrounding the apparatus (Chapter VII.), a fairly constant temperature may be maintained. A rapid stream of water should be employed, and if a large quantity of water is allowed to flow away from a tap on the service pipe beyond the point at which the jacketing water is taken off, variations in the temperature due to draughts, etc., are avoided.

Any desired temperature may be obtained by passing the water through a coil immersed in a water-bath.

The whole apparatus can often be immersed in an Ostwald thermostat (*Physico-Chemical Measurements*), which can be made for the purpose out of a large beaker. The temperature may in this way be maintained constant within 0.1 C. for some weeks. Baths of fused salts, such as mixtures of sodium and potassium nitrates, well stirred by a mechanical stirrer, may be employed in working at higher temperatures; Jena glass beakers must be employed in the latter case.

The temperature of a pure liquid boiling under constant pressure remains fairly constant, but there is often a tendency towards superheating, as in the case of liquid nitrogen. The temperature of the

vapour is usually more definite, but vapour-jackets can only be employed in the case of substances which are liquids at the normal temperature. The following very simple methods have been applied by Ramsay and Young to the production of constant and definite temperatures above that of the atmosphere. Fig. 132 shows the apparatus employed in heating the bulb A of a gas thermometer. The stem of the thermometer passes through a cork, which is covered by a layer of mercury to protect it from the action of the liquid which is boiled in the flask B; the vapour is condensed in the tube C. To regulate the pressure the apparatus is connected with a flask of about two litres capacity, and with a manometer E. The pressure in the apparatus can be adjusted by means of an air-pump connected with F. The temperature of the vapour in A is directly determined from the observed pressure (p. 319).

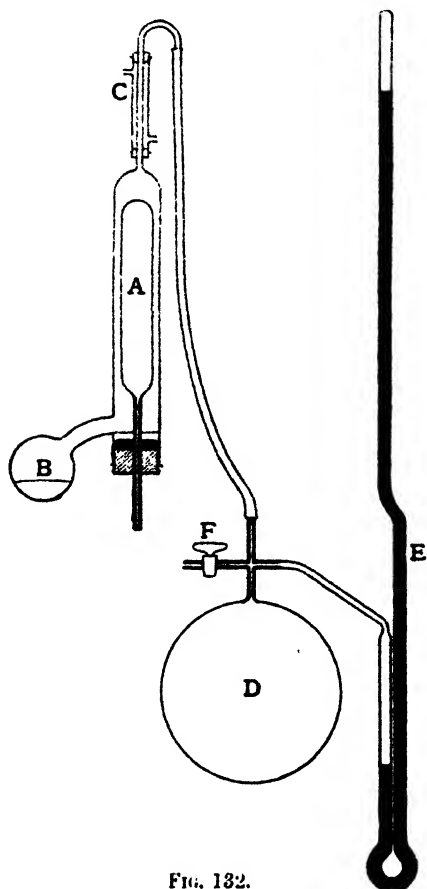


FIG. 132.

It is very much more difficult to maintain a constant temperature by boiling a liquefied gas under a pressure considerably below the normal; this may, however, be done in the apparatus described in Chapter XVI. The gas is first liquefied in the tube surrounding the

apparatus to be cooled by immersing it in liquid air, and is then evaporated by an exhaust-pump, or by connecting the tube containing it with another immersed in liquid air. The method is not, however, satisfactory unless a considerable quantity of liquid can be obtained.

Kammerlingh Onnes has paid particular attention to the methods for maintaining liquid ethylene and other gases at a constant temperature. His work is described in the *Proceedings of the Amsterdam Academy* (published in English), but involves the use of apparatus which is only to be found in his own laboratory. A simple calculation will indicate the size of the pump required to evaporate 500 c.c. of liquid air in an hour under a pressure of 10 mm.

If pure anhydrous ether, contained in a large vacuum-vessel, is mixed with liquid air, it may be cooled down to  $-120^{\circ}\text{C}$ . without becoming solid. If the vacuum-vessel is a good one the temperature rises very slowly, and the bath may be employed in the determination of critical points, etc. The bath should be stirred by means of a rotating screw, and the temperature may be determined by means of a gas or resistance thermometer. It has already been pointed out that the thermo-electric couple gives very erratic results when used to measure low temperatures.

## TABLES OF BOILING-POINTS

(1) CARBON DISULPHIDE.—Range from  $0^{\circ}$  to  $50^{\circ}$ .

T.	P.	T.	P.	T.	P.	T.	P.
0 <sup>o</sup>	127.9	13 <sup>o</sup>	224.95	26 <sup>o</sup>	374.95	39 <sup>o</sup>	596.85
1	133.85	14	234.4	27	389.2	40	617.5
2	140.05	15	244.15	28	403.9	41	638.7
3	146.45	16	254.25	29	419.0	42	660.5
4	153.1	17	264.65	30	434.6	43	682.9
5	160.0	18	275.4	31	450.65	44	705.9
6	167.15	19	286.55	32	467.15	45	729.5
7	174.6	20	298.05	33	484.15	46	753.75
8	182.25	21	309.9	34	501.65	47	778.6
9	190.2	22	322.1	35	519.65	48	804.1
10	198.45	23	334.7	36	538.15	49	830.25
11	207.0	24	347.7	37	557.15	50	857.1
12	215.8	25	361.1	38	576.75		

(1) ETHYL ALCOHOL.—Range from  $40^{\circ}$  to  $79^{\circ}$ .

T.	P.	T.	P.	T.	P.	T.	P.
40 <sup>o</sup>	133.7	50 <sup>o</sup>	220.0	60 <sup>o</sup>	350.3	70 <sup>o</sup>	541.2
41	140.75	51	230.8	61	366.4	71	564.35
42	148.1	52	242.05	62	383.1	72	588.35
43	155.8	53	253.8	63	400.4	73	613.2
44	163.8	54	265.9	64	418.35	74	638.95
45	172.2	55	278.6	65	437.0	75	665.55
46	181.0	56	291.85	66	456.35	76	693.1
47	190.1	57	305.65	67	476.45	77	721.55
48	199.65	58	319.95	68	497.25	78	751.0
49	209.6	59	334.85	69	518.85	79	781.45

(1) Regnault, *Mémoires*, vol. 26, pp. 394 and 349; Ramsay and Young, *Journ. Chem. Soc.*, vol. 47, p. 640.



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